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Van der Waals Forces

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A. INTRODUCTION AND HISTORY

RECENT theoretical developments explaining the nature of the forces between molecules have produced a variety of successful applications so numerous and extensive as perhaps to call for a more detailed review of the relevant basic facts than has previously been given. An excellent and authoritative summary of the essentials of both theory and applications has been presented at a meeting of the Faraday Society by F. London,[1] and many points of interest have arisen in the subsequent discussion of that paper.[2] The present article, while mainly limited in its scope to the theory, is intended to be a more comprehensive and analytic account of the elements of this important field, and to include material which has come to light since the publication of London's report.

The term "van der Waals force" is not one of very precise usage. A definition which seems to reflect its most widely adopted meaning, and to which the present discussion will adhere, is this: Van der Waals force is that force which gives rise to the constant a in van der Waals equation. It will be recalled that the latter equation contains a volume constant, b, which is related to the "size" of the molecules or, in a more refined statistical theory, to the intermolecular distance at which the attractive forces become strongly repulsive; in addition to this it involves the pressure constant a which measures the specific strength of the interactions with which we are here concerned. Our definition sets them apart on the one hand from chemical forces arising out of interpenetration of electron clouds and the resulting rearrangements governed by the Pauli principle, on the other hand from ionic interactions, both of which are sometimes included under the more general heading of intermolecular forces. The latter two are here excluded from consideration, not because they are unimportant, but for methodical reasons. The manner of calculating them is quite different from that employed for van der Waals forces, and as to the repulsive forces, the general methods available are not sufficiently accurate at present to make their review worth while.

The existence of van der Waals forces was known long before the famous work of Diderik van der Waals. They first entered the scene of physical investigation in connection with the work of Borelli and Jurin on capillary action. To explain their findings, they postulated attractive forces between the molecules of the tube walls and of the liquid. But it was soon pointed out by Clairault[3] that if these forces were the cause of surface tension their action must be general, embracing all molecules, though molecules of different kinds with different intensities.

From there on the development of the subject bears a close and fascinating resemblance to the present groping after an explanation of nuclear forces. First, general theories not specifying the exact form and nature of the forces are developed. Then specific assumptions as to their range and their dependence on distance are tried, without very definite conclusions: the exact form of the forces did not appear to matter greatly, experimental facts were not precise enough to distinguish. All through this period, lasting from the beginning to the end of the nineteenth century, investigators were convinced of the novelty and essential uniqueness of these forces which existed in addition to the Coulomb law of gravitational attraction and had a much smaller range but greater strength within that range. The final solution was in a sense an anticlimax; the forces were ultimately stripped of their uniqueness and shown to be of the nature of simple electric interactions.

Laplace's[4] genius provided the mathematical theory by which it was possible to show that if the forces acted along the lines joining the molecules and had a short range, they would produce a surface tension depending on curvature in the way observed. Gauss[5] refined and extended Laplace's theory. Maxwell[6] was the first to attempt specification of the law of interaction. On analyzing the none-too-accurate experimental data on viscosity and diffusion velocities of gases, particularly their dependence on temperature, he concluded (1) that the forces are repulsive, and (2) that they are proportional to $1/R^5$. Later developments have substantiated neither of these conclusions which, even at the time, stood in definite contradiction to the porous plug experiment of Joule and Kelvin, performed in 1853. Next, van der Waals,[7] without specifying his forces any more than to regard them as attractive, succeeded in deriving his equation of state and in deepening, through his conception of these forces, the understanding of many phases of physical chemistry.*

Speculations as to the exact nature of van der Waals forces arise again when Boltzmann,[8] taking up Maxwell's researches, investigates their range and space dependence. Though his work on this particular problem has not proved as fruitful as his other achievements, it is of some interest today because of its close alignment with present inquiries. One of Boltzmann's models for van der Waals attraction is indeed the three-dimensional potential pot with vertical walls, at present of nuclear fame. He concludes

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* It may be of interest to theorists in nuclear physics that van der Waals, in some of his researches, used a potential of the form $V=Ae^{-r/a}/r$.

that it, among others, is capable of explaining the then known facts.

The most extensive work on a special force law has been done by W. Sutherland.[9] His endeavor was to apply the law of attraction, $F=Am_1m_2/R^4$, which was suggested to him originally by a study of Laplace's work, to as many different experimental data as possible. In his formula, m_1 and m_2 are the masses of the two interacting molecules, and A is a parameter varying from substance to substance. With his force law he succeeds in explaining the Joule-Kelvin effect and, of course, capillary action. Later, and this fact is very interesting in view of modern evidence (cf. Section C–I), he establishes a general correlation between the parameter A and the atomic polarizabilities of the substances involved, and even attempts an analysis of intermolecular forces in terms of molecular structure. The singularity at $R=0$, inherent in Sutherland's formula, is not troublesome in his investigations because he never permits his molecules to come very close to each other.

This general line of attack, which starts from a force law assumed *ad hoc* and analyzes experimental data in terms of its parameters, has been continued, with refinements and generalizations, by Lennard-Jones[10] and his pupils. By means of a law of the form

$$F=\lambda R^{-n}-\mu R^{-m}, \tag{1}$$

in which the first term represents a repulsive and the second the van der Waals force ($n>m$, so that the range of the repulsive forces is smaller than for the attractive), he penetrates the field of statistical mechanics and correlates such different fields as virial coefficients and viscosities. Useful as this procedure has proved to be, its detailed discussion is beyond the scope of this article, for Eq. (1) is now known to be unsuited as an accurate theoretical expression for intermolecular forces.

The quest for an explanation of van der Waals forces in terms of more basic matters seems to have been initiated by Reinganum[11] who points out that neutral molecules carrying localized charges repel or attract each other with forces varying more rapidly with distance than $1/R$. This force is on the average attractive because of the torques tending to rotate the molecules into attractive positions. The elaboration of this idea is due to Keesom.[12] He considers as his simplest case molecules bearing dipoles. The forces between dipoles, which will be studied in greater detail below, are well known from electrostatics; their average over all orientations is zero. Thus if all molecules were rotating without regard for each other, and with random phase relations, no mean attraction for the bulk of them would result. As a matter of fact, however, the molecules do feel each other's presence; attractive relative orientations, having smaller potential energies and hence greater statistical weight, predominate and thus produce on the whole attraction. Looking at this effect more closely, we observe it to be the consequence of two conflicting tendencies, one of which outweighs the other. Molecules having sufficient rotational kinetic energy will rotate faster, and hence spend less time in attractive positions, than in others. This reduces the statistical weight under discussion. It will frequently happen, however, that a molecule, as a result of a collision, will be caught in an attractive position, i.e., in a position of dipole alignment with another molecule, with so little rotational energy that it can no longer rotate but must oscillate. This state of affairs continues until another impact occurs, and it is this possibility of temporary alignment which endows attractive forces with their greater weight. This effect is often referred to as Keesom's effect of alignment (*Richteffekt*) or orientation effect. It produces a *mean* interaction energy between two molecules of dipole moments p_1 and p_2 proportional to $p_1^2p_2^2/R^6$, where R is the distance between the molecular centers.

Obviously, this effect cannot provide a general explanation of van der Waals forces for two simple reasons. First, many molecules, exhibiting attractive forces, are known to possess no dipole moments; second, the orientation effect becomes inappreciable at high temperatures because the trapping of molecules with high kinetic energy is unlikely; but van der Waals forces persist. Keesom attempted to remove the first difficulty by applying his theory to quadrupoles (cf. below for an exact definition), i.e., to charge distributions of greater symmetry than dipoles, yet not spherically symmetrical and hence producing an external field. Quadrupole moments cannot be measured directly, but it is to be inferred from their known structure that many molecules must possess quadrupole distributions. Putting his theory in reverse, Keesom was then able to compute for various molecules certain constants characterizing the quadrupole distribution which would produce the observed van der Waals forces. We note in this connection a rather remarkable coincidence, well fitted to asperse the significance of exact numerical agreement in computations: Keesom, using a theory now regarded as inadequate, arrived at a value of 2.03×10^{-26} e.s.u. for the constant in question for H_2, while Burger,[13] using the now equally obsolete Bohr-Debye model for H_2, had calculated the value 2.05×10^{-26} e.s.u. for the same constant. The Heitler-London theory leads to 0.39×10^{-26} e.s.u.[14]

Keesom's theory gave reasonable values for the quadrupole moments of molecules according to contemporary standards; it was in need of extension only because of its failure to produce van der Waals forces at temperatures for which the effect of alignment is negligible. This defect was removed by Debye,[15] who called attention to the fact that molecules are not rigid structures but deformable distributions of charge. If placed in an external field, they will become polarized, and forces of attraction will be called into play if the field is non-uniform, as in the case of soft iron placed near the pole of a magnet. This fact at once accounts for the universal character of van der Waals forces and for their persistence at high temperatures, for polarization forces are always attractive, and their magnitude is independent of the molecule's state of motion. The only question is: what produces the polarizing field? Here again, quadrupoles had to be postulated. Debye first calculates the field, **F**, at a distance **R** from a quadrupole molecule. A molecule with polarizability α, if placed in this field, will suffer a change in energy given by

$$V=-\tfrac{1}{2}\alpha F^2. \tag{2}$$

To obtain the mean energy of interaction it is necessary to integrate V over all orientations of the field-producing molecule, and this procedure leads to

$$V_{\text{Av}}=3\alpha\tau^2/2R^8, \tag{3}$$

in which τ is related to the quadrupole moments, Θ_i;* thus,

$$\tau^2=\Theta_1{}^2+\Theta_2{}^2+\Theta_3{}^2-(\Theta_1\Theta_2+\Theta_1\Theta_3+\Theta_2\Theta_3). \tag{4}$$

Of interest is the fact that the interaction energy due to the present effect, often termed the *induction* effect, varies with $1/R^8$ (for quadrupoles as polarizing structures).

In order to connect his theory with observations Debye supposes that each field-producing molecule contributes an energy of interaction given by (3), and hence integrates that expression over the positions of all molecules. By comparing the result with experiments on deviations from Boyle's law he is then enabled to calculate the needed values of τ. These range all the way from 2.8 to 60×10^{-26} e.s.u. for different molecules. Debye's theory of the induction effect was extended to dipole gases by Falkenhagen,[16] who worked out the second virial coefficient, and included in his calculation also the effect of alignment.

It will be observed from Eq. (4) that τ is zero if the three principal quadrupole moments of a molecule are equal. This will certainly be the case when its charge distribution is nearly spherical. It is now well known that molecules possessing closed shells, and in particular rare gas atoms, possess this high degree of symmetry, and hence should display no van der Waals attractions. Yet they do, indeed so strongly that Debye was led to postulate $\tau=18.9\times10^{-26}$ e.s.u. for Xe. An equally serious difficulty with the alignment theory comes to light when we consider that the phenomenon of alignment concerns essentially no more than two molecules. If three are interacting closely, the forces will not in general have the property of additivity. (Cf. Section C–IV.) Forces caused by the induction effect *are* additive as one may see as follows.

If the field is due to n molecules distributed at random, V is no longer given by (2), but by

$$V=-\tfrac{1}{2}\alpha\Big(\sum_{i=1}^{n}\mathbf{F}_i\Big)^2.$$

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* A definition of the Θ_i is given in Section B–I.

In the next step, when a mean is taken over all orientations of the polarizing molecules, terms like $\langle \mathbf{F}_i \cdot \mathbf{F}_j \rangle_{\text{Av}}$ will vanish and the sum reduces to n squares all of which are equal. Hence, finally, if $\langle V_1 \rangle_{\text{Av}}$ is the energy due to one molecule,

$$V_{\text{Av}} = n \langle V_1 \rangle_{\text{Av}}$$

and this implies additivity. It is true that the molecules will not be oriented quite at random, but this lack of randomness is temperature-dependent. Hence the slight nonadditive part of the induction forces is also temperature-dependent. It is usually neglected in the theory.

Up to this point, then, the situation may be described briefly thus: Keesom's alignment effect is capable of explaining van der Waals forces in dipole and quadrupole gases at low temperatures; Debye's induction effect introduces an additional attraction for such gases, an attraction which persists at high temperatures. Neither effect throws any light on the forces between rare gas atoms. In fact, if both effects are treated on the basis of our present knowledge of molecular structure, they may be shown to contribute jointly only a fraction of the observed van der Waals force even for dipole gases.*

It is thus apparent that an essential effect is missing, a general effect present also for spherical molecules, and possessing the property of additivity. A first suggestion of it appeared in a paper by Wang,[17] who calculated by quantum mechanical methods the interaction between two H atoms for large separation. His method is somewhat indirect and his result numerically inexact, but it shows that, in first approximation, these forces vary with R^{-7}, and that they are attractive. In 1930 London[18] recognized the fuller meaning of these forces, derived formulas for their calculation, and pointed out an intimate connection between their nature and the process of optical dispersion. For this reason the effect was termed by London the *dispersion effect*, a designation which is now common in the literature. Together with the numerous researches for which its discovery has opened the field, it will form the object of our discussions below.

The physical meaning of the dispersion effect may be described as follows. Consider two H atoms, sufficiently far apart so that their electron clouds do not overlap. These clouds are known to have spherical symmetry about the protons. Hence, if they represented *static* distributions of charge, one would have no influence on the other. But the electrons move, for they have kinetic energy even in their lowest "stationary" state. This means that each atom is momentarily a dipole, capable of inducing in the other an additional dipole moment parallel to itself. If the classical picture were permitted, one would say that the two electrons have a tendency to rotate in phase, and that this tendency competes with the disorganizing effect of the zero-point kinetic energies. And although the average dipole moment over a large number of revolutions is zero, the tendency of alignment persists and causes attractive forces. Those who can still read mechanical pictures into mathematical developments will perceive that the derivation in Section C rests upon this intuitive situation.

Though the dispersion effect is of greater interest in most applications, alignment and induction among polar molecules are also of importance. In the following section we shall develop the theory of specific interactions between polar molecules, but shall omit the dispersion effect. The first part is a more mathematical presentation of matters already discussed qualitatively in this introduction, the second deals with the modifications brought about in classical results by an application of quantum mechanics.

B. FORCES BETWEEN POLAR MOLECULES

I. Classical theory of interactions

Since the meaning of multipoles is fundamental to the entire analysis we begin by discussing it in some detail. Let us consider a system of point charges, e_i, distributed at various points $\mathbf{r}_i$. The potential at an external point, a distance $\mathbf{R}$ from the origin, is given by $\phi = \sum_i e_i / |\mathbf{R} - \mathbf{r}_i|$. If this expression is expanded in a Taylor series in which the coordinates of all $\mathbf{r}_i$ are considered smaller than R, the result is

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* The value of the second virial coefficient of NH_3, for instance, computed on the basis of these two effects, is less than half of the observed value at all temperatures for which observations exist.

$$\varphi=\frac{\sum e_i}{R}+\frac{1}{R^2}\left(\frac{X}{R}\sum e_ix_i+\frac{Y}{R}\sum e_iy_i+\frac{Z}{R}\sum e_iz_i\right)$$
$$+\frac{1}{R^3}\left[\frac{1}{2}\left(\frac{3X^2}{R^2}-1\right)\sum e_ix_i^2+\frac{1}{2}\left(\frac{3Y^2}{R^2}-1\right)\sum e_iy_i^2\right.$$
$$+\frac{1}{2}\left(\frac{3Z^2}{R^2}-1\right)\sum e_iz_i^2+\frac{3XY}{R^2}\sum e_ix_iy_i$$
$$\left.+\frac{3XZ}{R^2}\sum e_ix_iz_i+\frac{3YZ}{R^2}\sum e_iy_iz_i\right]+\cdots \quad (1)^*$$

This may be written in more compact form:

$$\varphi=q\cdot\frac{1}{R}+\sum_\rho p_\rho\frac{\partial}{\partial X_\rho}\cdot\frac{1}{R}$$
$$+\frac{1}{2!}\sum_{\rho\sigma}\Theta_{\rho\sigma}\frac{\partial}{\partial X_\rho}\frac{\partial}{\partial X_\sigma}\cdot\frac{1}{R}+\cdots \quad (2)$$

if we define $X_1=X$, $X_2=Y$, $X_3=Z$;

$$q=\sum e_i;\quad p_1=\sum e_ix_i,\quad p_2=\sum e_iy_i,\ \text{etc.};$$
$$\Theta_{11}=\sum e_ix_i^2,\quad \Theta_{12}=\sum e_ix_iy_i,\ \text{etc.} \quad (3)$$

q is the total charge, p a vector known as the dipole moment; $\boldsymbol{\Theta}$ is a tensor of the second rank called the quadrupole moment. The best definition of the latter is in terms of the present analysis: it represents a certain set of coefficients appearing in the expansion of the potential of an arbitrary distribution of charges. Eq. (3) shows that the quadrupole moment is analogous to the moment of inertia of a mass distribution. Higher multipole moments would be defined by an extension of (2). The characteristic feature of dipoles is that their potential is proportional to $1/R^2$; quadrupoles produce a potential proportional to $1/R^3$; octupoles, to $1/R^4$, etc., as is seen from (1). The first term of (1) is zero, of course, if the charge distribution is on the whole neutral.

To understand the choice of names we observe that if two point charges of opposite signs are placed a certain distance apart, the first term of the potential vanishes but all others remain. If the distance between them is made infinitesimal while the charges increase correspondingly, all higher terms are small compared to the second, and this alone represents the potential. Such a distribution is a dipole. A way to make the first *two* terms of (2) (and no others) vanish is to arrange four charges on the corners of a parallelogram, with the signs of the charges alternating as one goes around the parallelogram, for this insures that the centroid of the positive charges coincides with that of the negative charges. On shrinking the dimensions of the figure while increasing the charges, the third term remains dominant; this arrangement is known as a quadrupole. Eight point charges on the corners of a parallelepiped, alternating in sign as one goes around any face of it, constitute an octupole. Such a structure has the property that the "moment of inertia" of the positive charges is equal to that of the negative charges about any axis, and this means that all components of the quadrupole moment vanish; the fourth term in (2) (not written) is the first to remain, and it is the only one if the octupole has very small dimensions.

Θ has in general six components, but it behaves like an ordinary moment of inertia inasmuch as it is always possible to choose the coordinate system in such a way that $\Theta_{ij}=0$ if $i\neq j$. This fact reduces Θ to three principal components, Θ_1, Θ_2, and Θ_3, to which attention may always be restricted.

It is frequently forgotten that the vanishing of the quadrupole moments is not a ***necessary*** condition for the absence of a quadrupole potential. Inspection of Eq. (1) shows the term in R^{-3} to be zero if only the three principal quadrupole moments are equal. This case is of far greater interest in molecular physics than that of charge distributions, like the octupole, which have no quadrupole moments. Thus one should properly say that an atom with closed shells possesses quadrupole moments, but produces no quadrupole potentials. The terminology relating to this point is not always precise.

For some purposes it is convenient to write Eq. (2) in terms of surface spherical harmonics, so that it reads

$$\varphi=\sum_{n=0}^{\infty}\frac{1}{R^{n+1}}\sum_i e_ir_i^nP_n(\cos\theta_i).$$

Here θ_i is the angle which $\mathbf{r}_i$ makes with $\mathbf{R}$.

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* The equations of each section, A, B, C, etc. are numbered independently.

However, we shall not have occasion to make use of this expression.

To obtain the basic expression for the classical interaction of two molecules it is necessary to calculate the energy which results when a second distribution of charges is put at the place where the potential is $\varphi(\mathbf{R})$. Let this distribution be characterized by charges ϵ_j, placed at distances $\boldsymbol{\rho}_j$ from a new origin which is itself displaced a distance $\mathbf{R}$ from the origin with respect to which the $\mathbf{r}_i$ were reckoned. The interaction energy is then given by

$$V=\sum{}_j\epsilon_j\varphi(\mathbf{R}+\boldsymbol{\rho}_j). \tag{4}$$

This expression in its expanded form is in general quite complicated; we will simplify it at once by introducing some obvious conditions. First, we suppose that both charge distributions are neutral; second, that one kind of charge, say the positive, is all localized at a point, and this point will be taken as origin for each distribution; third, that all $\rho_j<R$ as was already supposed for the r_i. The last assumption permits a development of (4) in a Taylor series:

$$\begin{aligned}V=&\sum_j\epsilon_j\cdot\varphi+\sum_j\epsilon_j\left(\xi_j\frac{\partial\varphi}{\partial X}+\eta_j\frac{\partial\varphi}{\partial Y}+\zeta_j\frac{\partial\varphi}{\partial Z}\right)\\&+\tfrac{1}{2}\sum_j\epsilon_j\left(\xi_j{}^2\frac{\partial^2\varphi}{\partial^2 X}+\cdots+2\eta_j\zeta_j\cdot\frac{\partial^2\varphi}{\partial Y\partial Z}\right)+\cdots\\=&\left\{q'+\sum_\rho p_\rho{}'\frac{\partial}{\partial X_\rho}\right.\\&\left.+\frac{1}{2!}\sum_{\rho\sigma}\Theta_{\rho\sigma}{}'\frac{\partial}{\partial X_\rho}\frac{\partial}{\partial X_\sigma}+\cdots\right\}\varphi(R).\end{aligned} \tag{4'}$$

In the last row we have used the same symbolism as in (2), but the primed quantities now refer to the second molecule. If (1) is inserted in (4′) and the differentiations are carried out, there results the following expression[19] which is at the basis of the entire theory of van der Waals forces:

$$\begin{aligned}V=&-\frac{1}{R^3}\sum_{ij}e_i\epsilon_j(2z_i\zeta_j-x_i\xi_j-y_i\eta_j)\\&+\frac{3}{2R^4}\sum_{ij}e_i\epsilon_j[r_i{}^2\zeta_j-z_i\rho_j{}^2+(2x_i\xi_j+2y_i\eta_j-3z_i\zeta_j)(z_i-\zeta_j)]\\&+\frac{3}{4R^5}\sum_{ij}e_i\epsilon_j[r_i{}^2\rho_j{}^2-5z_i{}^2\rho_j{}^2-5r_i{}^2\zeta_j{}^2-15z_i{}^2\zeta_j{}^2+2(4z_i\zeta_j+x_i\xi_j+y_i\eta_j)^2]+\cdots.\end{aligned} \tag{5}$$

In writing V in this form, both the z_i and ζ_j axes are taken along the intermolecular distance $\mathbf{R}$. The three rows of (5) represent, respectively, the dipole, dipole-quadrupole, and quadrupole energy. Higher terms have not been considered. If they are of importance, the present mode of approach through Taylor series is best abandoned. It is to be noted that (5) is valid only if all r_i and ρ_j are smaller than R, and rapid convergence will occur only if they are considerably smaller. This means that none of the charges of the two molecules may overlap. It is this condition which sets off the treatment of van der Waals forces from that of chemical forces, and makes the former relatively simple.

(*a*) *Dipole alignment*

A particularly interesting example is the interaction between molecules in which the charges may be regarded as fixed, so that the molecules can only move and rotate as wholes. Furthermore, let us assume the molecules to be *linear* structures. If we specify the directions of the two axes with respect to R by $\theta_1\varphi_1$ and $\theta_2\varphi_2$, then, for instance, $\sum_i e_i z_i=p_1\cos\theta_1$ if p_1 is the dipole moment of molecule 1 along its axis, and $\sum_i e_i z_i{}^2=\Theta_1\cos^2\theta_1$ etc., if Θ_1 is the component of quadrupole moment of molecule 1 along its axis. Note that here each molecule can be characterized by a single component of Θ, and that the subscripts 1 and 2 now refer, not to different components as before, but to the two molecules. A simple model of a linear molecule having both p and Θ is represented in Fig. 1. (If $r_1=r_2$, p vanishes but Θ remains.) Under these conditions, then, Eq. (5) takes the form

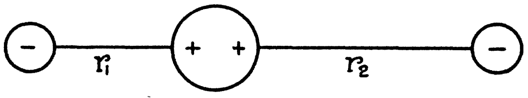

FIG. 1. Linear molecule.

$$
\begin{aligned}
V= & -(p_1p_2/R^3)[2\cos\theta_1\cos\theta_2-\sin\theta_1\sin\theta_2\cos(\varphi_1-\varphi_2)] \\
& +(3/2R^4)\{\Theta_1p_2[\cos\theta_2+2\cos\theta_1\sin\theta_1\sin\theta_2\cos(\varphi_1-\varphi_2)-3\cos^2\theta_1\cos\theta_2] \\
& \qquad -\Theta_2p_1[\cos\theta_1+2\cos\theta_2\sin\theta_1\sin\theta_2\cos(\varphi_1-\varphi_2)-3\cos^2\theta_2\cos\theta_1]\} \\
& +(3/4R^5)\Theta_1\Theta_2\{1-5\cos^2\theta_1-5\cos^2\theta_2-15\cos^2\theta_1\cos^2\theta_2 \\
& \qquad +2[4\cos\theta_1\cos\theta_2+\sin\theta_1\sin\theta_2\cos(\varphi_1-\varphi_2)]^2\}+\cdots. \qquad (6)
\end{aligned}
$$

This formula was used in the calculations of Keesom.[12]

It will be noticed that the mean of (6) taken over all orientations of either one of the molecules is zero, if all orientations are considered as equally likely. Were it not for the effect of the Boltzmann factor, which favors the lower energies, no mean van der Waals attraction would arise from the interaction of multipoles. Thus we must compute, not V_{Av}, but $\langle Ve^{-V/kT}\rangle_{\text{Av}}$, in which the average is taken over all orientations of both molecules. This quantity may be written on expansion of the exponential:

$$V_{\text{Av}}-\langle V^2\rangle_{\text{Av}}/kT+\cdots.$$

Thus, since V_{Av} is zero, we see that the mean potential energy is negative and hence the force attractive; also that it vanishes for large T.

The computation of $\langle V^2\rangle_{\text{Av}}$ is easy if we remember that

$$\langle\cos^2\theta\rangle_{\text{Av}}=\tfrac{1}{3};\quad \langle\sin^2\theta\rangle_{\text{Av}}=\tfrac{2}{3};\quad \langle\cos^2(\phi_1-\phi_2)\rangle_{\text{Av}}=\tfrac{1}{2};$$

$$\langle\sin^2\theta\cos^2\theta\rangle_{\text{Av}}=2/15;\quad \langle\cos^4\theta\rangle_{\text{Av}}=1/5;$$

$$\langle\sin^4\theta\rangle_{\text{Av}}=8/15;\quad \langle\cos^4(\phi_1-\phi_2)\rangle_{\text{Av}}=\tfrac{3}{8}.$$

We find

$$-\frac{\langle V^2\rangle_{\text{Av}}}{kT}=-\frac{1}{kT}\left[\frac{2}{3}\frac{p_1{}^2p_2{}^2}{R^6}+\frac{\Theta_1{}^2p_2{}^2+\Theta_2{}^2p_1{}^2}{R^8}+\frac{14}{5}\frac{\Theta_1{}^2\Theta_2{}^2}{R^{10}}+\cdots\right]-\frac{1}{(kT)^2}[\quad]\cdots. \qquad (7)$$

This expression is the first approximation to the weighted mean of V, i.e., to $\langle Ve^{-V/kT}\rangle_{\text{Av}}$.

If a molecule has a dipole moment of sufficient magnitude, one may usually neglect all but the first term of (7); if it has no dipole moment, the third term is the first to be finite. The second term is either zero or, if finite, of secondary importance. For this reason it has always been neglected in the literature on polar molecules. But there are undoubtedly many cases, perhaps not of interest at the moment, for which the second term should be considered.

Clearly, Eq. (7) is correct only as long as the expansion $e^{-V/kT}$ may be restricted to the first two terms. For temperatures of the order of V_{max}/k and smaller it has no validity at all. The physical reason for its failure is the preponderance at low temperatures of states of impeded rotation (libration). It would be possible, of course, to calculate $\langle Ve^{-V/kT}\rangle_{\text{Av}}$ for this case also, but the result would have no meaning. For the impeded motion, being quantized, differs so strongly from its classical description that the present methods may not be employed in studying it.

(*b*) *Induction effect*

Having discussed Keesom's alignment theory, let us now consider the Debye-Falkenhagen induction effect. The potential due to a single molecule at **R** is given by (1) which may be written conveniently for the present purpose

$$\varphi=\frac{1}{R^3}\mathbf{R}\cdot\mathbf{p}-\frac{1}{2R^5}\mathbf{M}\cdot\boldsymbol{\Theta}$$

if we introduce two convenient vectors **M** and **Θ** whose components are defined by $M_x=R^2-3X^2$, etc., $\Theta_x=\Theta_1$, etc.; $\Theta_{ij}=0$ if $i\neq j$. The field at R is

$$\mathbf{F}=-\nabla\varphi=-\frac{\mathbf{p}}{R^3}+\frac{3}{R^5}\mathbf{R}\cdot\mathbf{p}\mathbf{R}+\frac{\mathbf{N}}{R^5}-\frac{5}{2R^7}\mathbf{M}\cdot\boldsymbol{\Theta}\mathbf{R}, \qquad (8)$$

where **N** is a new vector having components $N_x=(\Theta_y+\Theta_z-2\Theta_x)X$, etc. N_y and N_z are formed by cyclical permutation of x, y and z. The induced energy is

$$V=-\tfrac{1}{2}\alpha F^2.$$

The *mean* energy in which we are interested is obtained by taking the mean of F^2 over all orientations of the molecule. But we may equally well calculate it by keeping the molecule fixed and taking a similar average over all orientations of $\mathbf{R}$. In this process we can treat $\mathbf{p}$ and $\boldsymbol{\Theta}$ as constant vectors. Squaring (8) and omitting quantities which vanish in the mean, we get

$$F^2=\frac{p^2}{R^6}+\frac{3}{R^8}(\mathbf{R}\cdot\mathbf{p})^2+\frac{N^2}{R^{10}}+\frac{25}{4R^{12}}(\mathbf{M}\cdot\boldsymbol{\Theta})^2-\frac{5}{R^{12}}(\mathbf{M}\cdot\boldsymbol{\Theta})(\mathbf{N}\cdot\mathbf{R}).$$

But

$$\langle(\mathbf{R}\cdot\mathbf{p})^2\rangle_{\mathrm{Av}}=R^2p^2/3\,;\quad\langle N^2\rangle_{\mathrm{Av}}=2R^2\tau^2\,;$$

$$\langle(\mathbf{M}\cdot\boldsymbol{\Theta})^2\rangle_{\mathrm{Av}}=4R^4\tau^2/5\,;\quad\langle(\mathbf{M}\cdot\boldsymbol{\Theta})(\mathbf{N}\cdot\mathbf{R})\rangle_{\mathrm{Av}}=4R^4\tau^2/5.$$

Hence $$\langle F^2\rangle_{\mathrm{Av}}=2p^2/R^6+3\tau^2/R^8. \tag{9}$$

Here τ is the quantity already introduced in the previous section:

$$\tau^2=\Theta_1{}^2+\Theta_2{}^2+\Theta_3{}^2-\Theta_1\Theta_2-\Theta_1\Theta_3-\Theta_2\Theta_3.$$

The mean interaction energy due to polarization of one molecule by another is thus seen to be

$$-\alpha(p^2/R^6+3\tau^2/2R^8+\cdots). \tag{10a}$$

In general, an electric moment will also be induced in the polarizing molecule by the one at $\mathbf{R}$. If the two are of the same kind, the total energy is twice as great; otherwise the quantities referring to the different molecules must be distinguished, and the total potential energy becomes

$$V_{\mathrm{Av}}=-\alpha_1\left(\frac{p_2{}^2}{R^6}+\frac{3}{2}\frac{\tau_2{}^2}{R^8}+\cdots\right)-\alpha_2\left(\frac{p_1{}^2}{R^6}+\frac{3}{2}\frac{\tau_1{}^2}{R^8}+\cdots\right). \tag{10}$$

In this approximation, the effect is independent of the temperature. Strictly speaking, it would have been necessary to calculate again $\langle Ve^{-V/kT}\rangle_{\mathrm{Av}}$. Eq. (10) is the first term of this. The second, which introduces the temperature, is $\langle -V^2/kT\rangle_{\mathrm{Av}}$. It is proportional to R^{-12} and higher powers of R^{-1} and need not be considered. But this consideration shows that (10), too, loses its validity at temperatures not satisfying $T>V/k$.

II. Quantum mechanical theory

The theory which we are about to present is in large part due to London[20] who studied the interaction of dipoles by means of what he called the method of *unscharfe Resonanz*. This seemingly unfamiliar method, however, is simply a form of ordinary perturbation theory which may equally well be used in the treatment of the problem.

The general procedure is this: If it is desired to find the potential energy between two molecules, the first step is to determine their *classical* interaction. This is always given by Eq. (5). But it may not be needed in this general form. For instance, if the structures are rigid dipoles, one may employ (6), and if they have no quadrupoles, only the first line of that expression need be retained. The next step is to find the quantum mechanical mean of V, and this usually differs from the classical mean. It is done by what is known as a perturbation (or sometimes by a variation) calculation.

Let ψ_k be the state function describing the two molecules in their unperturbed state. If it is nondegenerate, the perturbation energy is given (in familiar notation) by

$$\Delta E=\Delta E_1+\Delta E_2+\cdots=V_{kk}+\sum_i{}'\frac{|V_{ki}|^2}{E_k-E_i}+\cdots. \tag{11}$$

In this connection, a remark on the relation between this and the classical V_{Av} may be illuminating. In the case of rotating dipoles, the classical V is a function of orientation; there is no unique value of V associated with a given state of rotation. In quantum mechanics, however, every (nondegenerate) state k of rotation has associated with it a definite interaction energy, and this is ΔE_k. The calculation of ΔE, as seen above, involves features reminiscent of the classical averaging process, in which $|\psi|^2$ takes the place of the constant classical weight factor. Statistically, the quantity $\Delta E_k e^{-\Delta E_k/kT}$ corresponds to the classical $\langle Ve^{-V/kT}\rangle_{\mathrm{Av}}$. At this stage of the calculation, there is frequently very little resemblance between the two corresponding quantities. But when, in further pursuits of the matter not included in this review, the quantities

$\Delta E e^{-\Delta E/kT}$ and $\langle V e^{-V/kT}\rangle_{\mathrm{Av}}$ are summed and integrated, respectively, over all possible states of motion, the results show a general similarity.[21] In fact it may be shown that for sufficiently high temperatures they are exactly equal in all cases. In this article we shall rarely go beyond the stage of calculating ΔE, the rest being a concern of statistical mechanics to be dealt with in applications of van der Waals forces.

When the function ψ representing the unperturbed state is degenerate, and has n components ψ_i, ΔE is no longer given by (11) but by the n roots of the determinant

$$|V_{ij}-\Delta E\delta_{ij}|=0, \tag{12}$$

in which V_{ij} are the matrix elements of V between the various ψ_i. The diagonal elements V_{kk} appearing in (11) usually vanish when V_{Av} is zero, but there are exceptions to this rule.

a. Rigid linear dipoles.—For this case, V is given by the first term of (6);

$$V=(p_1p_2/R^3)[\sin\theta_1\sin\theta_2$$
$$\times(\cos\varphi_1\cos\varphi_2+\sin\varphi_1\sin\varphi_2)-2\cos\theta_1\cos\theta_2].$$

The two molecules are in states characterized by quantum numbers l_1m_1 and l_2m_2, and the state function representing the two in their unperturbed condition (far apart) is a product of two surface spherical harmonics*

$$\psi_k=\psi(l_1m_1,\,l_2m_2)=P(l_1m_1,\,\cos\theta_1)$$
$$\times P(l_2m_2,\,\cos\theta_2)e^{i(m_1\varphi_1+m_2\varphi_2)},$$

where the P functions are associated Legendre polynomials. This state is degenerate with all others having the same value of l_1 and l_2, but different m_1 and m_2. Hence our problem is to calculate the roots of

$$|(l_1m_1l_2m_2|V|l_1\mu_1l_2\mu_2)-\Delta E\delta_{\mu m}|=0. \tag{13}$$

One may easily show, however, that all the matrix elements of V occurring here are zero, so that we get no first-order effect. The second-order energy, in accordance with (11), is

$$\Delta E_2=\sum_{\lambda_1\mu_1\lambda_2\mu_2}\frac{|(l_1m_1l_2m_2|V|\lambda_1\mu_1\lambda_2\mu_2)|^2}{E(l_1)+E(l_2)-E(\lambda_1)-E(\lambda_2)}. \tag{14}$$

Unless an external magnetic field is applied there is no way of specifying the values of m_1 and m_2. One is therefore rarely interested in ΔE_2 as it stands, but rather in its average over all magnetic quantum numbers. Since all values of m_1 and m_2 are equally probable and there are $(2l_1+1)(2l_2+1)$ of them, the quantity to be computed is

$$\langle\Delta E_2\rangle_{\mathrm{Av}}=(2l_1+1)^{-1}(2l_2+1)^{-1}\sum_{m_1m_2}\Delta E_2. \tag{14a}$$

It involves a summation over *all* magnetic quantum numbers, both in the initial and final states of the matrix elements, and this circumstance simplifies the result very much.

We first turn our attention to the calculation of the elements $(l_1\cdots|V|\cdots\mu_2)$. They involve the matrix elements of trigonometric functions between the states of a rotator, which are well known and will be listed here to facilitate reference.

$$\left.\begin{aligned}
\xi_{lm,\,\lambda\mu}&=(\sin\theta\cos\varphi)_{lm,\,\lambda\mu}\\
&=\tfrac{1}{2}A(m)\delta_{\mu,\,m+1}-\tfrac{1}{2}A(-m)\delta_{\mu,\,m-1},\\
\eta_{lm,\,\lambda\mu}&=(\sin\theta\sin\varphi)_{lm,\,\lambda\mu}\\
&=(1/2i)A(m)\delta_{\mu,\,m+1}\\
&\qquad+(1/2i)A(-m)\delta_{\mu,\,m-1},\\
\zeta_{lm,\,\lambda\mu}&=(\cos\theta)_{lm,\,\lambda\mu}=B\delta_{\mu,\,m};\\
&\text{where}\\
A(\pm m)&=\left[\frac{(l\pm m+2)(l\pm m+1)}{(2l+1)(2l+3)}\right]^{\frac{1}{2}}\delta_{\lambda,\,l+1}\\
&\qquad-\left[\frac{(l\mp m-1)(l\mp m)}{(2l+1)(2l-1)}\right]^{\frac{1}{2}}\delta_{\lambda,\,l-1}\\
B&=\left[\frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}\right]^{\frac{1}{2}}\delta_{\lambda,\,l+1}\\
&\qquad+\left[\frac{(l+m)(l-m)}{(2l+1)(2l-1)}\right]^{\frac{1}{2}}\delta_{\lambda,\,l-1}.
\end{aligned}\right\} \tag{15}$$

---

* To avoid double subscripts quantum numbers will frequently be written in parenthesis, together with arguments. It will be convenient to deal similarly with matrix elements: the Dirac notation is used interchangeably with the more common one; thus

$$(ijk|V|lmn)\equiv V_{ijk,\,lmn}.$$

In terms of these,

$$
\begin{aligned}
&(l_1m_1l_2m_2|\,V\,|\lambda_1\mu_1\lambda_2\mu_2)\\
&\quad=\frac{p_1p_2}{R^3}\{(l_1m_1|\,\xi\,|\lambda_1\mu_1)(l_2m_2|\,\xi\,|\lambda_2\mu_2)\\
&\qquad+(l_1m_1|\,\eta\,|\lambda_1\mu_1)(l_2m_2|\,\eta\,|\lambda_2\mu_2)\\
&\qquad\quad-2(l_1m_1|\,\zeta\,|\lambda_1\mu_1)(l_2m_2|\,\zeta\,|\lambda_2\mu_2)\}.
\end{aligned}
$$

On squaring this, there will arise cross terms like

$$(l_1m_1|\,\xi\,|\lambda_1\mu_1)(l_1m_1|\,\eta\,|\lambda_1\mu_1)^*,\text{ etc.}$$

These may be dropped at once for they vanish when the summation, indicated in (14), is performed over μ_1 and μ_2† and finally an average over all m_1 and m_2 in accordance with Eq. (14a) is taken. This can be seen from Eqs. (15). Moreover,

$$\sum_\mu|\,\xi_{lm,\,\lambda\mu}|^2=\sum_\mu|\,\eta_{lm,\,\lambda\mu}|^2=\tfrac{1}{4}[A^2(m)+A^2(-m)];$$

$$\sum_\mu|\,\zeta_{lm,\,\lambda\mu}|^2=B^2.$$

Simple calculation, and use of the fact that

$$\langle m^2\rangle_{\mathrm{Av}}\equiv(2l+1)^{-1}\sum_{-l}^{l}m^2=\tfrac{1}{3}l(l+1), \tag{15a}$$

leads to

$$
\begin{aligned}
\langle A^2\rangle_{\mathrm{Av}}&\equiv(2l+1)^{-1}\sum_m A^2\\
&=\frac{2}{3(2l+1)}[(l+1)\delta_{\lambda,\,l+1}+l\delta_{\lambda,\,l-1}];
\end{aligned}
$$

$$\langle B^2\rangle_{\mathrm{Av}}=\tfrac{1}{2}\langle A^2\rangle_{\mathrm{Av}}.$$

Because of these relations

$$
\begin{aligned}
&\sum_{m_1m_2,\,\mu_1\mu_2}|\,(l_1m_1l_2m_2|\,V\,|\lambda_1\mu_1\lambda_2\mu_2)\,|^2\\
&\quad=\frac{2}{3}\frac{p_1^2p_2^2}{R^6}\frac{1}{(2l_1+1)(2l_2+1)}\\
&\qquad\times[(l_1+1)\delta(\lambda_1,l_1+1)+l_1\delta(\lambda_1,l_1-1)]\\
&\qquad\times[(l_2+1)\delta(\lambda_2,l_2+1)+l_2\delta(\lambda_2,l_2-1)].
\end{aligned}\tag{16}
$$

Thus far the summation could be performed without considering the denominator in (14). The energy of a single rotator is

$$E_l=\tfrac{1}{2}l(l+1)\epsilon \tag{17}$$

with $\epsilon=\hbar^2/I$, and I its moment of inertia. The presence of four δ-functions in (16) indicates that the sum in (14) reduces to four terms. If the energies in the denominator are inserted in accordance with (17), the result will be

$$
\begin{aligned}
\langle\Delta E_2\rangle_{\mathrm{Av}}&=-\frac{2}{3}\frac{p_1^2p_2^2}{R^6}\frac{1}{(2l_1+1)(2l_2+1)}\\
&\quad\times\left\{\frac{(l_1+1)(l_2+1)}{(l_1+1)\epsilon_1+(l_2+1)\epsilon_2}+\frac{(l_1+1)l_2}{(l_1+1)\epsilon_1-l_2\epsilon_2}\right.\\
&\quad\left.+\frac{l_1(l_2+1)}{-l_1\epsilon_1+(l_2+1)\epsilon_2}-\frac{l_1l_2}{l_1\epsilon_1+l_2\epsilon_2}\right\}\\
&=-\frac{2}{3}\frac{p_1^2p_2^2}{R^6}\frac{1}{(2l_1+1)(2l_2+1)}\\
&\quad\times\left\{\left(\frac{\epsilon_1}{l_2+1}+\frac{\epsilon_2}{l_1+1}\right)^{-1}+\left(\frac{\epsilon_1}{l_2}+\frac{\epsilon_2}{l_1+1}\right)^{-1}\right.\\
&\quad\left.-\left(\frac{\epsilon_1}{l_2+1}-\frac{\epsilon_2}{l_1}\right)^{-1}-\left(\frac{\epsilon_1}{l_2}+\frac{\epsilon_2}{l_1}\right)^{-1}\right\}.
\end{aligned}\tag{18}
$$

This expression is valid for any two molecules having different p's and ϵ's. If the two molecules are of the same kind, (18) reduces to[20]

$$
\begin{aligned}
\langle\Delta E_2\rangle_{\mathrm{Av}}&=-\frac{2}{3}\frac{p^4I}{\hbar^2R^6}\\
&\times\frac{l_1(l_1+1)+l_2(l_2+1)}{(l_1+l_2)(l_1+l_2+2)(l_1-l_2-1)(l_1-l_2+1)}\cdots.
\end{aligned}\tag{19}
$$

Clearly, (18) and (19) do not hold under two conditions: (1) when $l_2\epsilon_2=(l_1+1)\epsilon_1$; (2) when $(l_2+1)\epsilon_2=l_1\epsilon_1$; for then the interaction becomes infinite. These cases are interesting for the following reason. Under condition (1) molecule 2 has a quantum number** $l_2=(l_1+1)\epsilon_1/\epsilon_2$ and may therefore emit a quantum of energy $2(l_1+1)\times(\epsilon_1/\epsilon_2)\cdot\epsilon_2$, which is precisely the quantum that molecule 1 would absorb if it passed from the state l_1 to l_1+1. The two are capable of ex-

---

* See footnote p. 10.

† Note that the denominator of (14) does not depend on μ.

** This can be exactly true only if ϵ_1/ϵ_2 or its reciprocal is an integer; but even if it is nearly true (18) becomes invalid, for $\langle\Delta E_2\rangle_{\mathrm{Av}}$ may then be so large that the perturbation method must be suspected.

changing energy, much like two pendulums in a state of resonance, and this terminology is generally applied to the present situation. Similarly, condition (2) amounts to the existence of resonance between the two molecules, but with molecule 1 in the "excited" and 2 in the absorbing state. If, however, such interchange of energy were actually to take place, it would be impossible for us to say in general which molecule contains the quantum and which is about to receive it, except perhaps at a given instant. Therefore our initial undertaking of allotting quantum numbers to the individual interacting partners was unwarranted, and that is the reason for the failure of (18) and (19). The case of resonance will be treated in the next section.

In terms of quantum mechanics, inability to specify individual quantum numbers implies degeneracy (of the state concerned!) and this is found in connection with conditions (1) and (2), for if the two molecules have quantum numbers l_1 and l_2 given in terms of a fixed l by the relations $l_1=l-1$, and $l_2\epsilon_2=(l_1+1)\epsilon_1$, they have the same total energy as for $l_1=l$; $(l_2+1)\epsilon_2=l_1\epsilon_1$, namely, $l^2(\epsilon_1+\epsilon_2)\epsilon_1/\epsilon_2$. To be consistent, $\langle\Delta E_2\rangle_{\mathrm{Av}}$ should, in the case of resonance, be averaged not only over all orientations (over m_1 and m_2) but over these two cases of resonance as well. When this is done, however, the singular terms having opposite signs in the two cases cancel out, and a finite answer results. Eq. (19) then takes the form

$$(\text{resonance})\langle\Delta E_2\rangle_{\mathrm{Av}}=-\frac{1}{6}\frac{p^4I}{\hbar^2R^6}\frac{4l^4-l^2+1}{(4l^2-1)^2}. \quad (19\text{a})$$

Of greatest practical importance is the interaction of similar molecules. Let us see when it is attractive and when repulsive. We find (19a) is always negative, (19) only when $l_1=l_2$ (the resonance condition $|l_2-l_1|=1$ being barred). Hence the rule: The average force (average over all magnetic quantum numbers) between dipoles is repulsive if their rotational quantum numbers differ by 2 or more, otherwise it is attractive.

For large differences $|l_2-l_1|=\Delta$, (19) may be written

$$\langle\Delta E_2\rangle_{\mathrm{Av}}\rightarrow\frac{1}{3}\frac{p^4I}{\hbar^2R^6}\frac{1}{\Delta^2-1}.$$

Table I. (*After London*). *Coefficient of $2p^4I/3\hbar^2R^6$ in Eqs. (19).*

l_1	$l_2=0$	1	2	3	4
0	−0.5	−0.111	0.25	0.100	0.0555
1	−0.111	−0.5	−0.0678	0.194	0.0786
2	0.25	−0.0678	−0.5	−0.0645	0.181
3	0.10	0.194	−0.0645	−0.5	−0.0336
4	0.0555	0.0786	0.181	−0.0336	−0.5

Table I, taken from London's paper, gives the coefficients of $2p^4I/3\hbar^2R^6$ occurring in (19).

In using the expressions for $\langle\Delta E_2\rangle_{\mathrm{Av}}$ considerable caution is necessary. Perturbation theory fails when the perturbation becomes comparable to the zero-order energies or their differences, as formula (11) clearly shows. But the rotational energy differences of molecules are small, and this fact sets a definite limit to the applicability of the expressions thus far derived. Rarely are they to be trusted for intermolecular distances smaller than 7A. What happens as the molecules approach more closely?

The answer to this question is of interest chiefly for situations in which the interaction is strong, for otherwise the validity of Eq. (19) extends to sufficiently small values of R. A glance at Table I shows this to be true for pairs of molecules having identical rotational quantum numbers. Now if $l_2=l_1>0$, there will be attraction, but the unperturbed energy may not be lowered beyond bounds even for very small R because the levels below l_1 will not permit it.* But when $l_2=l_1=0$ interesting things may happen since there is then no such limitation.

Let us, then, investigate the interaction for $l_2=l_1=0$. To treat this case it is necessary to use a method free from the limiting conditions of the perturbation theory. The variational method is well suited to the present purpose. We include in our calculation, besides the function representing the state in question (ψ_0), all those with which it will combine. Thus we take

$$\psi=c_0\psi_0+c_1\psi_1+c_2\psi_2+c_3\psi_3$$

with

$$\psi_0=Y_0^0(1)Y_0^0(2),\quad \psi_2=Y_1^{-1}(1)Y_1^1(2),$$
$$\psi_1=Y_1^0(1)Y_1^0(2),\quad \psi_3=Y_1^1(1)Y_1^{-1}(2),$$

---

* A fuller discussion of this effect is given by London. Its mathematical meaning is simply that the roots of the secular equation to which a variational treatment leads, will repel since they may not cross over each other.

where $Y_l^m(1)\equiv P(lm, \cos\theta_1)e^{im\varphi_1}$ as previously defined. The total energy operator $H=H_0+V$, in which V is the dipole part of Eq. (6). Now it is well known that $E=\int\psi^*H\psi d\tau/\int\psi^*\psi d\tau$ is equal to or greater than the true energy of the problem, and if we minimize E with respect to $c_0\cdots c_3$, we shall have obtained the best approximation attainable with the above functions, and in the present instance that is rather good. Minimization of E leads to the secular equation

$$|H_{ij}-E\delta_{ij}|=0, \tag{20}$$

of which $E_{\min}$ is the lowest root. H_{ij}, of course, is $\int\psi_i^*H\psi_j d\tau=E_i^0\delta_{ij}+V_{ij}$, and $E_0^0=0$, while $E_1^0=E_2^0=E_3^0=2\epsilon$ (cf. Eq. (17)). Furthermore, the V_{ij}, calculated from Eqs. (15), are easily seen to be 0, with the exception of

$$V_{01}=-\tfrac{2}{3}a,\quad V_{02}=V_{03}=-\tfrac{1}{3}a;\quad V_{ij}=V_{ji};\quad a=p^2/R^3.$$

Since $E_0^0=0$, E is the same as ΔE, the interaction energy we wish to compute. With these results, Eq. (20) takes the form

$$\begin{vmatrix} -\Delta E & -\frac{2}{3}a & -\frac{1}{3}a & -\frac{1}{3}a \\ -\frac{2}{3}a & 2\epsilon-\Delta E & 0 & 0 \\ -\frac{1}{3}a & 0 & 2\epsilon-\Delta E & 0 \\ -\frac{1}{3}a & 0 & 0 & 2\epsilon-\Delta E \end{vmatrix}=0.$$

The determinant reduces at once by suitable addition of rows and columns, and yields the equation

$$\left(\Delta E+\frac{4a^2/9}{2\epsilon-\Delta E}+\frac{2a^2/9}{2\epsilon-\Delta E}\right)(2\epsilon-\Delta E)^3=0,$$

whence

$$\Delta E+\frac{2}{3}\frac{a^2}{2\epsilon-\Delta E}=0,$$

so that

$$\Delta E=\epsilon\left[1-\left(1+\frac{2}{3}\frac{a^2}{\epsilon^2}\right)^{\frac{1}{2}}\right]$$

$$=\frac{\hbar^2}{I}\left[1-\left(1+\frac{2p^4I^2}{3\hbar^4R^6}\right)^{\frac{1}{2}}\right]. \tag{21}$$

For large values of R the radical in this formula may be expanded, and

$$\Delta E\rightarrow -p^4I/3\hbar^2R^6.$$

This agrees with (19) for $l_1=l_2=0$. For sufficiently small R, however,

$$\Delta E\rightarrow -(2/3)^{\frac{1}{2}}p^2/R^3. \tag{22}$$

The interesting feature in this result is the dependence of ΔE on R^{-3}. It recalls at once the fact that two dipoles, each in perfect alignment along R, have a classical potential energy $-2p^2/R^3$. One may therefore interpret the transition from an R^{-6} law to an R^{-3} law as the setting in of impeded rotation. The factor $(\frac{2}{3})^{\frac{1}{2}}$ in (22) may be too small since the latter is a variational result, but the correct factor is certainly smaller than 2 as is evident from the fact that the classical potential energy, $-2p^2/R^3$, is partly canceled by the zero-point kinetic energy of the oscillations. Analogy with the case of simple harmonic vibrations would lead one to expect a value near 1 for this factor; hence the limiting value ΔE given by (22) cannot be very much in error.

Resonance; general theory.—When the condition of resonance prevails between two interacting dipoles, an additional type of degeneracy is present and it becomes necessary to reinvestigate the *first*-order perturbation effect. It was seen in Section IIa that Eq. (13) was satisfied by $\Delta E=0$ because all $(l_1\cdots|V|\cdots\mu_2)$ vanish. The degenerate functions there included all those having fixed l_1 and l_2, but different m_1 and m_2. In the case of resonance (of like dipoles), where $l_1=l+1$, $l_2=l$, the class of degenerate functions is made up of those just mentioned plus all those with $l_1=l$, $l_2=l+1$ and all different m_1 and m_2. The degree of degeneracy is now twice as great, and we can no longer be sure that all V_{ij} are zero. Inspection will show that this is indeed not the case, and we expect a first-order effect, ΔE_1, to be superposed on the $\langle\Delta E_2\rangle_{\text{Av}}$ calculated in IIa. This first-order effect will be proportional to R^{-3} and therefore predominate at large distances of separation.

We wish to solve the equation $|V_{ij}-\Delta E_1\delta_{ij}|=0$ under these more general conditions. The elements V_{ij} divide into four groups in accordance with the classification above:

$$\begin{gathered}(l, m_1, l+1, m_2|V|l, \mu_1, l+1, \mu_2),\\ (l+1, m_1, l, m_2|V|l+1, \mu_1, l, \mu_2),\\ (l, m_1, l+1, m_2|V|l+1, \mu_1, l, \mu_2),\\ (l+1, m_1, l, m_2|V|l, \mu_1, l+1, \mu_2).\end{gathered}$$

The first group arises from states $l_1=l$, $l_2=l+1$

combining with each other; the second from states $l+1$, l combining with each other; the third and fourth from intercombinations between the two classes. The first two groups vanish, as before. This, of course, also implies the vanishing of all diagonal terms V_{ii}, which will be of interest later. The last two groups of V_{ij} are equal in pairs, and attention will at the moment be concentrated on the first of these.

We omit writing the fixed indices and abbreviate $(l,\ m_1,\ l+1,\ m_2|V|l+1,\ \mu_1,\ l,\ \mu_2)$ into $(m_1,\ m_2|V|\mu_1,\ \mu_2)$. Using again formulas (15) we find

$$\begin{aligned}(m_1,\ m_2|V|\mu_1,\ \mu_2)&=\frac{p^2}{R^3}\frac{1}{(2l+1)(2l+3)}\\ &\times\{-2[(l+m_1+1)(l-m_1+1)(l+m_2+1)\\ &\times(l-m_2+1)]^{\frac{1}{2}}\delta(\mu_1m_1)\delta(\mu_2m_2)\\ &+\tfrac{1}{2}[(l-m_1+2)(l-m_1+1)(l-m_2)(l-m_2+1)]^{\frac{1}{2}}\\ &\times\delta(\mu_1,\ m_1-1)\delta(\mu_2,\ m_2+1)\\ &+\tfrac{1}{2}[(l+m_1+2)(l+m_1+1)(l+m_2)(l+m_2+1)]^{\frac{1}{2}}\\ &\times\delta(\mu_1,\ m_1+1)\delta(\mu_2,\ m_2-1)\}\cdots.\end{aligned}\tag{23}$$

The problem now is to solve the secular equation after insertion of the above matrix elements. The result of this procedure cannot be generalized, for the roots turn out to be often irrational and exhibit little obvious regularity. A detailed investigation of special cases would have to start at this point. Our interest will be confined to the simple case: $l=0$. There are, however, a few general features of the first-order energy which may be derived on the basis of (23).

The total number of degenerate functions involved in the problem is $2\times(2l+1)(2l+3)$. This is the number of roots of the secular equation and hence the maximum number of levels into which a given state $(l,\ l+1)$ of the two molecules may split. Since most, though not quite all, of the roots may be shown to be double, the actual number of levels is about half as great. It is possible without difficulty to compute the *mean* value of all the levels, as well as their *root-mean-square* displacement. To see how this is done consider the equation

$$|V_{ij}-v\delta_{ij}|=0;\quad i,\ j=1,\ 2\cdots n.\tag{24}$$

The determinant may be expanded as follows:

$$\begin{aligned}|V_{ij}-v\delta_{ij}|&=(-v)^n+(-v)^{n-1}\sum_i V_{ii}\\ &+(-v)^{n-2}\sum_{i>j}(V_{ii}V_{jj}-V_{ij}^2)+\cdots.\end{aligned}\tag{25}$$

On the other hand, we observe that Eq. (24) may also be written in terms of its roots, v_1, v_2, $\cdots v_n$:

$$\prod_{i=1}^{n}(v-v_i)=0,$$

and this may be expanded

$$\begin{aligned}\prod_{i=1}^{n}(v_i-v)&=(-v)^n+(-v)^{n-1}\sum_i v_i+(-v)^{n-2}\\ &\cdot\tfrac{1}{2}[\sum_{ij}v_iv_j-\sum_i v_i^2]+\cdots.\end{aligned}\tag{26}$$

By equating coefficients of like powers of $-v$ in (25) and (26) we are at once led to the following useful relations:

$$\sum_i v_i=\sum_i V_{ii},\tag{27}$$

$$\sum_{ij}v_iv_j-\sum_i v_i^2=2\sum_{i>j}(V_{ii}V_{jj}-V_{ij}^2).\tag{28}$$

The first of these allows us to compute the mean of all the roots of our present problem. The v_i are now to be identified with the ΔE_1, the first-order energies. Since, as was already remarked, every V_{ii} vanishes, the mean of all ΔE_1 is zero. There is no resultant shift of the levels. This result is of importance because it means that the forces are just as likely to be attractive as repulsive, so that the resonance effect averages out in macroscopic situations involving dipoles in all possible states of interaction. A weighted average would retain only the squares of the roots and thus destroy the characteristic dependence on R^{-3}.

On substituting zero for $\sum_i v_i$ and also for every V_{ii} in Eq. (28) we find immediately

$$\sum_i v_i^2=2\sum_{i>j}V_{ij}^2,\tag{29}$$

a relation which allows us to calculate the sum of the squares of the roots.

According to (23)

$$2\sum_{i>j} V_{ij}^2 = 2 \sum_{m_1 m_2 \mu_1 \mu_2} (m_1, m_2 | V | \mu_1, \mu_2)$$

$$= \frac{p^4}{R^6} \frac{2}{(2l+1)^2(2l+3)^2} \sum_{m_1 m_2} \{4[(l+1)^2 - m_1^2][(l+1)^2 - m_2^2] + \tfrac{1}{4}[l^2 - 2lm_1 + 3l + m_1^2 - 2m_1 + 2] \times [l^2 - 2lm_2 + l + m_2^2 - m_2] + \tfrac{1}{4}[l^2 + 2lm_1 + 3l + m_1^2 + 2m_1 + 2] \times [l^2 + 2lm_2 + l + m_2^2 + m_2]\}.$$

The summation on the right of the first line is unrestricted although, on the left, half the V_{ij} are excluded. This results from the fact that on the right we are summing only over elements of the type l, $l+1 \rightarrow l+1$, l; the other half of the contribution to the sum comes from $l+1$, $l \rightarrow l$, $l+1$. When the summation is carried out in the last expression above, all terms having m_1 or m_2 as a factor drop out and we get, in view of Eq. (15a), and after combining terms,

$$2\sum_{i>j} V_{ij}^2 = \frac{4}{3} \frac{p^4}{R^6} (l+1)^2.$$

This, according to (29), is the sum of the squares of the roots ΔE_1. If we divide by $2(2l+1)(2l+3)$ and extract the square root we obtain the root mean square of the interaction energy:

$$[\langle (\Delta E_1)^2 \rangle_{\mathrm{Av}}]^{\frac{1}{2}} = \left(\frac{2}{3}\right)^{\frac{1}{2}} \frac{l+1}{[(2l+1)(2l+3)]^{\frac{1}{2}}} \frac{p^2}{R^3}. \tag{30}$$

Resonance; special case.—To consider a special case, let us compute the first-order forces between two dipoles with $l_1 = 0$, $l_2 = 1$. In forming the matrix elements according to (23) we observe that m_1 and μ_2 are now permitted only the value zero, and we get

$$(0, m_2 | V | \mu_1, 0) = \frac{1}{3} \frac{p^2}{R^3} \times [-2\delta(m_2 0)\delta(\mu_1 0) + \delta(m_2, -1)\delta(\mu_1, -1) + \delta(m_2, 1)\delta(\mu_1, 1)].$$

In forming the secular equation it must be remembered that the above element is an abbreviation for $(001m_2 | V | 1\mu_1 00)$ in our complete notation (cf. Eq. (13)). If the functions are labeled $\psi_1 \cdots \psi_6$ in the following order: (001–1), (1–100), (0010), (1000), (0011), (1100), this equation takes the simple form

$$\begin{vmatrix} -\Delta E_1 & \frac{1}{3}a & 0 & 0 & 0 & 0 \\ \frac{1}{3}a & -\Delta E_1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\Delta E_1 & -\frac{2}{3}a & 0 & 0 \\ 0 & 0 & -\frac{2}{3}a & -\Delta E_1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\Delta E_1 & \frac{1}{3}a \\ 0 & 0 & 0 & 0 & \frac{1}{3}a & -\Delta E_1 \end{vmatrix} = 0$$

and its roots are evidently

$$\Delta E_1 = \pm \frac{1}{3} \frac{p^2}{R^3}, \quad \pm \frac{2}{3} \frac{p^2}{R^3}. \tag{31}$$

The question now arises as to the relation between this first-order effect and the second-order effect expressed in Eq. (19). The latter already represents an average and therefore includes the present result whose mean is zero. If one were interested in the interaction of two dipoles in a definite magnetic state beyond the first-order approximation here derived, one would have to use a variational procedure and include in the formation of the secular determinant not only degenerate functions, as we have done, but also functions representing different energy states. If this were done we should find, for instance, that for small R the roots with positive sign in (31) would grow less rapidly than the others because there are roots corresponding to higher levels above but none below them.

London,[20] in his treatment of resonance, simplified the problem by including only a limited number of degenerate functions. He used only the functions (l, m_1, $l+1$, m_2), ($l+1$, m_1-1, l, m_2+1), ($l+1$, m_1, l, m_2), ($l+1$, m_1+1, l, m_2-1) and in that way obtained an expression for all the roots in closed form ($\pm a_4/R^3$ in his notation (cf. p. 274 of his paper)). That expression does not yield the correct positions of the roots of the complete secular equation, but may allow in many cases a useful approximation, for it has the same "root mean square" as the true solution.

The forces between rotating dipoles in individual quantum states have not been of wide interest because as a rule they are small in comparison with the dispersion forces, at least for the simpler molecules. One application to which the theory has lent itself thus far is the variation of line widths of HCN bands with rotational quantum number.[22]

b. Symmetric tops carrying dipoles

In classical theory, a rotating linear dipole molecule spreads its two charges over a complete circle and thereby annuls, in first approximation, its dipole moment. This is not necessarily true for a symmetrical top carrying a dipole along its figure axis. Thus one finds in that case a first-order interaction proportional to R^{-3} even though the two tops may not be in resonance states. Mathematically this comes about because the secular Eq. (13) corresponding to the case of tops contains nonvanishing elements V_{ij}. The details of the theory will not be presented here; they have been discussed in a paper by Warren and the author.[23] The ψ-functions are in this instance Jacobi polynomials, and the matrix elements V_{ij} can be computed easily from the known coordinate matrices of these functions. It turns out that the secular equation is rather similar in its structure to the one encountered with resonant dipoles. The forces are sometimes attractive and sometimes repulsive and have a vanishing mean. The root mean square is given by

$$[\langle\Delta E_1^2\rangle_{\mathrm{Av}}]^{\frac{1}{2}}=\left(\frac{2}{3}\right)^{\frac{1}{2}}\frac{K_1K_2}{J_1(J_1+1)J_2(J_2+1)}\frac{p^2}{R^3}, \qquad (32)$$

a formula which presents considerable similarity with Eq. (30). K and J are the usual quantum numbers of the symmetric top. It is interesting to note that the effect is zero when K_1 or $K_2=0$. All this is quite in line with what is known about the linear Stark effect.

The second-order energy, corresponding to Eq. (19) was given by K. G. Carroll;[24] it reads

$$\langle\Delta E_2\rangle_{\mathrm{Av}}=-\frac{2}{3}\frac{p^4}{R^6}\frac{I}{\hbar^2}\left\{\frac{(J_1+1)^2-K_1^2}{(J_1+1)(2J_1+1)}\left[\frac{(J_2+1)^2-K_2^2}{(J_2+1)(2J_2+1)(J_1+J_2+2)}+\frac{K_2^2}{J_2(J_2+1)(J_1+1)}+\frac{J_2^2-K_2^2}{J_2(2J_2+1)(J_1-J_2+1)}\right]\right.$$
$$+\frac{K_1^2K_2^2}{J_1(J_1+1)J_2^2(J_2+1)^2}$$
$$\left.+\frac{J_1^2-K_1^2}{J_1(2J_1+1)}\left[\frac{(J_2+1)^2-K_2^2}{(J_2+1)(2J_2+1)(J_2-J_1+1)}-\frac{K_2^2}{J_1J_2(J_2+1)}-\frac{J_2^2-K_2^2}{J_2(2J_2+1)(J_1+J_2)}\right]\right\}, \qquad (33)$$

where I is the moment of inertia about an axis transverse to the figure axis. This, too, reduces to (19) when $K_1=K_2=0$. But the effect (33) is generally smaller than (32).

c. Rigid linear quadrupoles

Two linear quadrupoles have a potential energy

$$V=(3/4R^5)\Theta_1\Theta_2[1-5\cos^2\theta_1-5\cos^2\theta_2+17\cos^2\theta_1\cos^2\theta_2+16\cos\theta_1\sin\theta_1\cos\theta_2\sin\theta_2\cos(\varphi_1-\varphi_2)+2\sin^2\theta_1\sin^2\theta_2\cos^2(\varphi_1-\varphi_2)], \qquad (34)$$

as may be seen from Eq. (6). The state functions are again spherical harmonics. In contradistinction to the case of linear dipoles, the present V gives rise to first-order energies, and makes an investigation of the secular equation necessary.

Let us consider a state (l_1m_1; l_2m_2), which is, of course, degenerate with all other values of

TABLE II. *Values of* $(\langle\Theta_3\rangle_{\mathrm{Av}}, \langle\Theta_1\rangle_{\mathrm{Av}})/er^2$ *for rotating linear dipoles.*

l	$m=-4$	-3	-2	-1	0	1	2	3	4
0					$(1/3, 1/3)$				
1				$(1/5, 2/5)$	$(3/5, 1/5)$	$(1/5, 2/5)$			
2			$(1/7, 3/7)$	$(3/7, 2/7)$	$(11/21, 5/21)$	$(3/7, 2/7)$	$(1/7, 3/7)$		
3		$(1/9, 4/9)$	$(1/3, 1/3)$	$(7/15, 4/15)$	$(23/45, 11/45)$	$(7/15, 4/15)$	$(1/3, 1/3)$	$(1/9, 4/9)$	
4	$(1/11, 5/11)$	$(3/11, 4/11)$	$(31/77, 23/77)$	$(37/77, 20/77)$	$(39/77, 19/77)$	$(37/77, 20/77)$	$(31/77, 23/77)$	$(3/11, 4/11)$	$(1/11, 5/11)$

m_1 and m_2. Through the first four terms of (34) this state will combine only with itself; through the fifth with $(l_1, m_1+1; l_2, m_2-1)$ and with $(l_1, m_1-1; l_2, m_2+1)$; through the last term it combines with itself, with $(l_1, m_1+2; l_2, m_2-2)$ and with $(l_1, m_1-2; l_2, m_2+2)$. Thus the secular equation contains both diagonal and nondiagonal elements, all of which must be considered in a complete treatment of the problem. But as is usual with the solution of secular equations, there is no general answer in closed form. We shall forego the rigorous task and present a simple approximate treatment, based on the observation that, after all, we find diagonal terms in this case and hence an opportunity to neglect the others. As a matter of fact the result thus derived is in general fairly reliable.

The problem is to calculate $(l_1, m_1, l_2, m_2|\,V\,|l_1, m_1, l_2, m_2)$. If we remember that the fifth term contributes nothing and that $\cos^2(\varphi_1-\varphi_2)$ may be replaced by $\frac{1}{2}$, the whole diagonal element may be written

$$(l_1, m_1, l_2, m_2|\,V\,|l_1, m_1, l_2, m_2) = \frac{3\Theta_1\Theta_2}{4R^5}\{2-6Z_1^2-6Z_2^2+18Z_1^2Z_2^2\}, \quad (35)$$

provided $Z_1^2 \equiv (l_1, m_1|\cos^2\theta_1|l_1, m_1)$ and a similar definition holds for Z_2^2. Now one may easily show that

$$Z^2 = \frac{2l^2+2l-1-2m^2}{(2l+3)(2l-1)},$$

and if this expression is substituted in (35) with subscripts properly attached, there results after a bit of algebraic simplification:

$$\Delta E_1 = \frac{6\Theta_1\Theta_2}{R^5} \times \frac{[l_1(l_1+1)-3m_1^2][l_2(l_2+1)-3m_2^2]}{(2l_1+3)(2l_1-1)(2l_2+3)(2l_2-1)}. \quad (36)$$

The main features of this result were stated by London.[18c] Two points are to be observed in connection with (36): first, ΔE_1 vanishes if one or both of the molecules are in the lowest rotational state $(l=0)$; second, if summed over all values of m_1 or of m_2, the expression for ΔE_1 vanishes. Hence there is no *mean* interaction in first order between two quadrupoles. Both of these characteristics are shared by the result of a complete treatment in which the nondiagonal terms are retained.

In addition to ΔE_1 there is also the second-order contribution ΔE_2 which is proportional to R^{-10}. To our knowledge this has never been calculated although for the case $l=0$ it is the only one present. But we shall see below that these quadrupole effects are in general (to be specific: for simple molecules) subordinate to other attractions, and for that reason they have attracted but little attention.

Effect (36) decreases with distance less rapidly than the second-order dipole effect (19). This becomes significant when we observe that rigid dipoles exhibit not only the attraction given by (19), but (36) as well. For a linear molecule is never truly a dipole, because its charges are not an infinitesimal distance apart and infinite, but separated by an amount not always inappreciable compared to the distance of approach of two molecules. Let us then investigate at what approximate distance of separation effect (36) begins to predominate for an ordinary rigid molecule.

The molecule may be idealized as two opposite point charges e a fixed distance r apart. For $l_1=l_2=1$ and $m_1=m_2=0$ as an example we obtain from (19) and (36)

$$\frac{|\Delta E_1|}{|\Delta E_2|_{\mathrm{Av}}} \doteq 3\frac{\Theta^2}{p^4}\frac{\hbar^2}{I}R.$$

We wish to find the value of R for which this expression is unity. Now $\Theta^2/p^4=1/e^2$ and $\hbar^2/I \approx 3$ or 4×10^{-15} ergs for actual simple molecules. Thus, if

$$(10^{-14}/e^2)R > 1, \qquad R > 2.5\times10^{-5} \text{ cm}.$$

But at these large distances one is rarely interested in the van der Waals forces. Besides, the quadrupole forces would be overshadowed by purely magnetic forces at these large distances. (Cf. Section C–V.)

It is interesting to note that interactions of the type (36) are present also between atoms whose normal states are not S states. As such they have been the subject of detailed treatment in a recent paper by Knipp.[25] He finds binding energies amounting to a sizeable fraction of a volt for interatomic distances of twice the atomic radii, which indicates a possibility of molecule formation ("*L* valences.")

A question to which we want to refer briefly is why the dipole-dipole energy vanishes in first order, whereas the quadrupole-quadrupole energy does not. Classically, a rotating linear dipole has no average dipole moment, and if its axis of rotation were equally likely to point in any direction, its quadrupole moments would be equal and produce no field. In quantum mechanics, the latter condition is true only if $l=0$, for then the ψ-function is a constant, and equal weight is assigned to all axes of rotation. If $l\neq 0$, that is no longer the case. Indeed one may easily show that in general a rotating linear dipole has different quadrupole moments along different directions.

The calculation merely involves the study of

$$\langle\Theta_1\rangle_{\mathrm{Av}}=\int (Y_l^m)^2 e\cdot x^2 d(\cos\theta),$$

and of $\langle\Theta_2\rangle_{\mathrm{Av}}$ and $\langle\Theta_3\rangle_{\mathrm{Av}}$, constructed similarly but with y^2 and z^2 in place of x^2. One finds that $\langle\Theta_1\rangle_{\mathrm{Av}}=\langle\Theta_2\rangle_{\mathrm{Av}}$ in general, but $\langle\Theta_3\rangle_{\mathrm{Av}}\neq\langle\Theta_1\rangle_{\mathrm{Av}}$ except in special cases. In Table II we list the values of $\langle\Theta_3\rangle_{\mathrm{Av}}$ and $\langle\Theta_1\rangle_{\mathrm{Av}}$ (in parentheses) for various l and m. The cross-elements Θ_{xy}, etc. vanish automatically with the customary choice of axes. The symbol r in the table represents the (fixed) displacement of the charges.

The average dipole moments computed in a similar manner, are clearly all zero. This explains why there is a first-order interaction with quadrupoles, but not with dipoles.

d. Induction effect

To treat the induction effect it becomes necessary to shift attention from rigid to deformable molecules. It will be shown that quantum mechanics leads to essentially the same formula as does classical physics. The matter is best discussed in connection with a simple model: two interacting dipoles, one of which is deformable (1), the other (2) rigid. The analysis then proceeds exactly as in Section (a) as far as Eq. (16). From there on, two things must be remembered: first, molecule (1) has, in addition to the closely spaced rotational energy levels, certain widely spaced levels which correspond to different vibrational or electronic states; second, p_1 is the same for all rotational levels belonging to one vibrational or electronic state, but must be treated as a variable, er, in general. The sum, $\sum_j{}'|V_{ij}|^2/(E_i-E_j)$, may be split into two, the first extending over all levels of molecule (2) and all *rotational* levels of molecule (1) associated with its lowest electronic or vibrational state in which we suppose it to be; the second extending over all other levels of molecule (1) and, of course, again over all levels of molecule (2). In the first sum, p_1^2 may be factored out as in (16), the sum yielding Eq. (19); but the second sum becomes:

$$\frac{2}{3}\frac{p_2^2}{R^6}\sum_{\kappa_1\lambda_2}{}'\frac{|(0|e\mathbf{r}_1|\kappa_1)|^2[(l_2+1)\delta(\lambda_2,l_2+1)+l_2\delta(\lambda_2,l_2-1)]}{[F(0)-F(\kappa_1)+E(l_2)-E(\lambda_2)](2l_2+1)}. \tag{37}$$

Here the index κ_1 labels all states of molecule (1) belonging to different electronic or vibrational levels than the lowest one, and $F(\kappa_1)-F(0)$ are the energy differences corresponding to these levels. These differences are in general much larger than $E(l_2)-E(\lambda_2)$; hence the latter may be neglected against them. When this is done, however, the summations referring to the two molecules may be carried out independently in (37), and it is seen that the one over λ_2 yields 1. Eq. (37) thus becomes

$$-\frac{2}{3}\frac{p_2^2}{R^6}\sum_{\kappa}{}'\frac{|(e\mathbf{r})_{0\kappa}|^2}{F_\kappa-F_0}.$$

If now we recall the well-known expression for the polarizability

$$\alpha=\frac{2}{3}\sum_{\kappa}{}'\frac{|(e\mathbf{r})_{0\kappa}|^2}{F_\kappa-F_0} \tag{38}$$

we see immediately that the effect in question produces

$$\langle \Delta E_2 \rangle_{\mathrm{Av}} = -\alpha_1 p_2^2/R^6 \tag{39}$$

which is identical with the first term of (10a). The entire expression (10a) would have followed if a quadrupole moment also had been ascribed to molecule (2), as the reader may verify by the same method. This result is of course quite general. Suppose, for instance, that molecule (2) has no dipole moment in its normal state. Then the entire first sum would have been absent, but Eq. (39) is unaltered.

C. Forces Between Nonpolar Molecules (Dispersion Forces)

I. Perturbation theory of dispersion forces

a. London's general formula

The second-order forces between polar molecules encountered so far are all caused by one or the other of the following two mechanisms: The rotating charges in the interacting molecules have a tendency to rotate in phase; or there is a momentary distortion of one molecule by the other, and this distortion is in phase with the motion of the charges in the molecule producing it. It is clear that these two causes are not limited in their operation to polar molecules but affect nonpolar ones as well.

Before presenting London's theory it is well to recall a few simple facts of radiation theory and atomic structure. The usual expression for the intensity of a spectral line corresponding to a transition from a state (k) to a state (κ), and also the dispersion formula, involve certain numerical constants known as f values or oscillator strengths, whose classical meaning is the number of electrons taking part in that particular transition. In quantum mechanics, this number is not usually integral. Let us first describe the transition $(k)\rightarrow(\kappa)$ more exactly. Among the quantum numbers denoted by (k) there is at least one, m, on which the energy of the state does not depend, except when an external field is applied. A similar quantum number, μ, exists for (κ). The f value, however, will in general depend on m and μ. It will also be different for different components of polarization of the light originating in the transition, or undergoing dispersion. Hence we define

$$f^{(x)}{}_{km,\,\kappa\mu} = \frac{2}{3}\frac{M}{\hbar^2}|X_{km,\,\kappa\mu}|^2(E_\kappa - E_k). \tag{1}$$

Here $X=\sum_i x_i$, the sum being extended over the positions of all electrons in the atom; M is the electron mass. $f^{(y)}$ and $f^{(z)}$ are defined similarly.

These f values are of interest only in Zeeman-effect observations. Usually one confines attention to the sum of the f's connecting a given state (km) with all the degenerate states of κ; moreover, since the m value of the initial state cannot be ascertained either, one takes a mean over all m. This leads to the definition

$$f^{(x)}{}_{k,\,\kappa} = \frac{1}{2L+1}\sum_{m,\,\mu} f^{(x)}{}_{km,\,\kappa\mu}; \tag{2}$$

where L is the quantum number of angular momentum for state k. Now one may show that in this process of summing, the dependence on polarization is lost:

$$f^{(x)}{}_{k,\,\kappa} = f^{(y)}{}_{k,\,\kappa} = f^{(z)}{}_{k,\,\kappa} \equiv \tfrac{1}{3} f_{k,\,\kappa}. \tag{3}$$

These relations are needed for the development which follows. We wish to point out that they are not restricted to one-electron atoms but are perfectly general. To be sure, spin effects have been neglected. They may, however, be included without changing the result we desire. In the following we treat multiplet states as a single state.

The classical interaction between two atoms or molecules is given by B (5). For the present only the first row of V will be retained since it yields the leading term at large distances. It may be written

$$V = (e^2/R^3)(X_1X_2 + Y_1Y_2 - 2Z_1Z_2), \tag{4}$$

the subscripts 1 and 2 referring to the two molecules in question. They are considered to be in states k_1 and k_2. The elements $(k_1m_1k_2m_2|V|k_1\mu_1k_2\mu_2)$ will in general not vanish, as we know from the last section. For atoms in S states, however, they are zero. Whether they are or not, the average over all degenerate states m_1 and m_2, in which we are chiefly interested at present, is always zero. Turning then to the second approximation of the perturbation theory, we find

$$\Delta E_2=\frac{e^4}{R^6}\sum_{\kappa_1\mu_1\kappa_2\mu_2}\frac{\begin{array}{l}|(k_1,m_1|X|\kappa_1,\mu_1)(k_2,m_2|X|\kappa_2,\mu_2)+(\cdots|Y|\cdots)(\cdots|Y|\cdots)\\ \qquad\qquad -2(\cdots|Z|\cdots)(\cdots|Z|\cdots)|^2\end{array}}{E(k_1)+E(k_2)-E(\kappa_1)-E(\kappa_2)}. \tag{5}$$

The summation over μ_1 and μ_2 may be performed without regard for the denominator, which does not depend on these quantum numbers. This is fortunate, for the summation over μ_1 and μ_2 annuls the cross terms arising when the numerator of (5) is squared. To see this, we consider $\sum_\mu X_{km,\kappa\mu}Y^*_{km,\kappa\mu}$. For X we write $R\sin\theta\cos\varphi$, where the important factor is $\cos\varphi$. Now the state function for the molecule, complicated as it may be, depends on φ only through the factor $e^{im\varphi}$. The sufficient condition for this dependence is axial symmetry of the Hamiltonian, and this will here be assumed. Hence

$$X_{km,\,\kappa\mu}=(R\sin\theta)_{km,\,\kappa\mu}\cdot\frac{1}{2\pi}\int\frac{e^{i\varphi}+e^{-i\varphi}}{2}e^{i(m-\mu)\varphi}d\varphi$$
$$=(R\sin\theta)_{km,\,\kappa\mu}\cdot\tfrac{1}{2}[\delta_{\mu,\,m+1}+\delta_{\mu,\,m-1}].$$

Similarly, one finds

$$Y_{km,\,\kappa\mu}=(R\sin\theta)_{km,\,\kappa\mu}\cdot\frac{1}{2i}[\delta_{\mu,\,m+1}-\delta_{\mu,\,m-1}].$$

The product of these two quantities obviously vanishes when summed over μ.

Thus far will the simplification of Eq. (5) proceed without further assumptions. If it is assumed that the molecules have spherical symmetry in states k_1 and κ_1,

$$\sum_\mu|X_{km,\,\kappa\mu}|^2=\sum_\mu|Y_{km,\,\kappa\mu}|^2$$
$$=\sum_\mu|Z_{km,\,\kappa\mu}|^2\equiv\tfrac{1}{3}|R_{k,\,\kappa}|^2$$

and these sums also become independent of m, so that

$$\Delta E_2=-\frac{2}{3}\frac{e^4}{R^6}\sum_{\kappa_1\kappa_2}{}'\frac{|(k_1|R|\kappa_1)|^2|(k_2|R|\kappa_2)|^2}{E(k_1)+E(k_2)-E(\kappa_1)-E(\kappa_2)}. \tag{6}$$

When this symmetry does not exist, a simple formula may be derived for the *mean* of ΔE_2 over all values of m_1 and m_2.

$$\langle\Delta E_2\rangle_{\text{Av}}=\frac{1}{2L_1+1}\frac{1}{2L_2+1}\sum_{m_1m_2}\Delta E_2=\frac{1}{2L_1+1}\frac{1}{2L_2+1}$$
$$\frac{e^4}{R^6}\sum_{\substack{\kappa_1\mu_1m_1\\ \kappa_2\mu_2m_2}}{}'\frac{\begin{array}{l}|(k_1m_1|X|\kappa_1\mu_1)|^2|(k_2m_2|X|\kappa_2\mu_2)|^2\\ \qquad +|(\cdots|Y|\cdots)|^2|(\cdots|Y|\cdots)|^2+4|(\cdots|Z|\cdots)|^2|(\cdots|Z|\cdots)|^2\end{array}}{E(k_1)+E(k_2)-E(\kappa_1)-E(\kappa_2)}.$$

When relations (1), (2) and (3) are used here, the result is

$$\langle\Delta E_2\rangle_{\text{Av}}=-\frac{3}{2}\frac{e^4}{R^6}\cdot\frac{\hbar^4}{M^2}\sum_{\kappa_1\kappa_2}\frac{f(k_1\kappa_1)f(k_2\kappa_2)}{[E(k_1)-E(\kappa_1)][E(k_2)-E(\kappa_2)][E(k_1)+E(k_2)-E(\kappa_1)-E(\kappa_2)]}. \tag{7}$$

This formula is quite general; it was first derived by London.[18c] It is applicable, of course, to the case where 1 and 2 are different kinds of molecules if $E(k_1)$ and $E(k_2)$ refer to the two different sets of levels and a similar distinction is made with respect to $f(k_1\kappa_1)$ and $f(k_2\kappa_2)$.

One interesting feature of van der Waals forces is at once apparent from (7). Suppose k_1 and k_2 denote the normal states of the molecules. Both f's are then positive, and $E(\kappa)>E(k)$. $\langle\Delta E_2\rangle_{\text{Av}}$ is then negative. Hence the general theorem regarding dispersion forces: Molecules in their normal states attract each other. The dominant part played in formula (7) by the "dispersion f values" has given the forces their name.

There is no essential difference between the forces here under discussion and other second-order van der Waals forces, for instance those expressed in Eqs. B(18), (19) and (33). They may all be written in the form (7). One can easily show with the use of Eqs. B(15) *et seq.* that for a rigid rotator

$$f(l,\lambda)=\frac{2}{3}\frac{1}{2l+1}\{(l+1)^2\delta_{\lambda,\,l+1}-l^2\delta_{\lambda,\,l-1}\}.$$

If this expression is substituted into (7), there results Eq. B(18). Even B(39) may be regarded as a special case of (7). To be consistent, therefore, we should apply the name "dispersion forces" to all second-order interactions, whether they refer to polar or nonpolar molecules.

The usefulness of the formulation in terms of f values lies in the circumstance that these are sometimes known from empirical dispersion formulas, whereas the matrix elements appearing in (6) etc. are usually difficult to calculate.

b. Special case: atomic hydrogen

For atomic hydrogen an exact theoretical evaluation of Eq. (7) is possible. f values have been calculated by Sugiura.[26] In performing the indicated summations the continuous energy states beyond the series limit must be included. When dealing with the nondegenerate normal state of H one may replace $\langle\Delta E_2\rangle_{\mathrm{Av}}$ by ΔE_2, and κ may be taken to be the principal quantum, n. Also, $E(\kappa)-E(k)=(1-1/n^2)(e^2/2a)$. Then

$$\Delta E_2=-\frac{12}{(R/a)^6}\frac{e^2}{a}$$

$$\times\sum_{n_1n_2}\frac{f(1n_1)f(1n_2)}{(1-n_1^{-2})(1-n_2^{-2})(2-n_1^{-2}-n_2^{-2})}.$$

On evaluating this sum numerically, Eisenschitz and London[18a] obtained

$$\Delta E_2=-\frac{6.47}{(R/a)^6}\frac{e^2}{a}.$$

Later calculation by a variation method[27] (cf. Section III) indicates that a more exact value of the constant is 6.499.

c. Approximate formulas

The f values needed in Eq. (7) can often be obtained from the empirical relation between index of refraction and frequency of light. The index of refraction, r, is expressible in terms of the polarizability α, in a familiar way: $(r^2+1)/(r^2+2)=(4\pi/3)(N/V)\alpha$. On the other hand, α is related to molecular constants through the dispersion formula:

$$\alpha_k=\frac{e^2\hbar^2}{M}\sum_\kappa\frac{f_{k\kappa}}{(E_\kappa-E_k)^2-h^2\nu^2}. \qquad (8)$$

The index (k) specifies the state of the molecule to which the polarizability refers. Eq. B(38), which defines the *static* polarizability for the ground state, is the special case of (8) for $\nu=0$. Much work has been done to correlate measurements of r for the entire range of visible frequencies with values of $f_{k\kappa}$ and of $E_\kappa-E_k$.[28] The tendency is, of course, to fit the data with as few terms in (8) as possible. In many instances this can indeed be done with sufficient accuracy in the measured range of r by using only a single f. This implies one of two things: either the f value corresponding to a single transition is very much greater than all others, or there is a small range of energies $E_\kappa-E_k$ to which the most intense transitions are confined. At any rate, one must not lose sight of the fact that the use of a single term dispersion formula is always an approximation valid only in a limited frequency range. All empirical material relating to Eq. (8) has reference to the normal state.

Suppose, then, that (8) contains but one term for which the energy difference is Δ. Let α^0 be the static polarizability. From (8),

$$f=(M/e^2\hbar^2)\Delta^2\alpha^0. \qquad (9)$$

If both molecules have one-term dispersion formulas, (7) may be written

$$\langle\Delta E_2\rangle_{\mathrm{Av}}=-\frac{3}{2R^6}\frac{\Delta_1\Delta_2}{\Delta_1+\Delta_2}\alpha_1{}^0\alpha_2{}^0, \qquad (10)$$

the subscripts here refer to the different molecules. In actual cases the quantities Δ are often nearly equal to the ionization energies of the molecules. For that reason formula (10) is sometimes used to estimate dispersion forces even when no dispersion data are known, by substituting ionization energies for the Δ's. Table III contains numerical values obtained with the use of (10) for a number of substances.

It often happens that a one-term dispersion formula is valid for one of the interacting partners, but not for the other. One is then entitled to substitute (9) in (7) for one of the molecules:

$$\langle \Delta E_2 \rangle_{\text{Av}} = -\frac{3}{2R^6}\frac{e^2\hbar^2}{M}\Delta_1 \alpha_1{}^0 \times \sum_{\kappa_2} \frac{f(k_2\kappa_2)}{[E(\kappa_2)-E(k_2)][E(\kappa_2)-E(k_2)+\Delta]}. \tag{11}$$

This formula is useful when it is desired to compute the forces between Hg and rare gas atoms which give rise to loosely bound van der Waals molecules,[18] and also in the calculation of the displacement of Hg spectrum lines by pressure of a foreign gas.[29]

The validity of Eqs. (7)–(11) is limited to large values of R. They are never correct at distances smaller than the sum of the gas kinetic diameters of the molecules, and indeed at this distance the terms corresponding to the last two lines of Eq. B (5) must be considered. A very exact treatment of these interactions is hardly warranted at present, however, because of the uncertainty in our knowledge of the exchange forces and of interpenetration which also become effective at these distances. We turn now to a simple consideration of dipole-quadrupole and of quadrupole-quadrupole contributions to the dispersion forces, first computed for H–H and for He–He interactions.[30]

d. Contribution of quadrupole interaction to dispersion forces

It is to be noted that the higher terms in B (5) give an effect not only in the case of molecules with quadrupole symmetry, but generally, even for spherical distributions of charge, and this for the same reason that the first term contributes when there is no permanent dipole moment. The present considerations are limited to the forces between two H and two He atoms in their normal states. Denoting now the whole of B (5) by V we have

$$\Delta E_2 = \sum_{\kappa_1\kappa_2}{}' \frac{|(00|V|\kappa_1,\kappa_2)|^2}{2E(0)-E(\kappa_1)-E(\kappa_2)}, \tag{12}$$

the index 0 here refers to the ground state. Being interested in an approximate answer, we make use of the following simplifying circumstance. For H, the first excited level lies $(1-1/2^2)$ times 13.5 volts above the normal state, hence all discrete excited levels lie between 10 and 13.5 volts. The continuous states beyond this limit, to be sure, extend to ∞, but their weight rapidly diminishes. For He, the case seems even more favorable, all discrete levels due to excitation of one electron lying between 20.5 and 24.5 volts above the ground state. Above these are doubly excited and continuous states of low weight. It seems plausible, therefore, to replace the denominator of (12) by a mean, $\langle -E \rangle_{\text{Av}}$, which one would expect to be in the neighborhood of twice the ionization potential. Thus

$$\Delta E_2 \doteq -\frac{1}{2E_{\text{Av}}}\sum_{\kappa_1\kappa_2}{}' |(00|V|\kappa_1,\kappa_2)|^2 = -\frac{(V^2)_{00,\,00}-(V_{00,\,00})^2}{2E_{\text{Av}}} \tag{13}$$

the last step by matrix algebra.* But $(V^2)_{00,\,00}$ involves only the state function for the ground state of this system, and this can be computed with relative ease. On the other hand, we already know that $V_{00,\,00}$ is zero. In computing V^2, cross terms which are odd in the coordinates of either atom 1 or 2 may at once be omitted for they would vanish in the integration over $[\psi_0(1)\psi_0(2)]$. When use is made of the spherical symmetry of ψ_0 and also of the separability of ψ_0 (for He) into factors, one for each electron (we shall use Slater functions in the calculation; cf. below), Eq. (13) turns into

$$\Delta E_2 = -\frac{2N^2}{3R^6}\frac{e^4}{E_{\text{Av}}}\left\{(r^2)_{00}{}^2+\frac{3}{R^2}(r^4)_{00}(r^2)_{00} + \frac{21}{5R^4}(r^4)_{00}{}^2+\cdots\right\}\cdots. \tag{14}$$

A distinction between the two atoms is here no

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* This is valid because the state functions with which the matrix elements are formed are a complete set.

longer necessary because they are assumed alike. The symbol N in this formula stands for the number of electrons in each atom.

For H, ψ_0 is known exactly; it is $2a^{-\frac{3}{2}}e^{-r/a}$. The matrix elements are easily computed: $(r^2)_{00}=3a^2$, $(r^4)_{00}=22.5a^4$. We define $R'\equiv R/a$, with $a=0.528$A, and we also recall that the ionization potential of H is $-E_0=e^2/2a$. Eq. (14) then reads, for hydrogen,

$$\Delta E_2=-\frac{24}{R'^6}\frac{E_0{}^2}{E_{\text{Av}}}\left\{1+\frac{22.5}{R'^2}+\frac{236}{R'^4}+\cdots\right\}\cdots. \tag{15}$$

We have already pointed out that E_{Av} should be about $-2E_0$. If this were substituted, the factor outside the brace would be $12E_0/R'^6=6e^2/R'^6a$. We know from Section (b) that the correct numerical factor is 6.5. This shows the extent to which our simple method is in error.

The van der Waals minimum for two H atoms comes at about $R'=6.5$. At this interatomic distance, the dipole-quadrupole term contributes about $\frac{1}{2}$, the quadrupole-quadrupole term about 1/7 as much as the first term alone.

Pauling and Beach,[27] using a much more elaborate variational method, obtained for the bracket expression

$$\left\{1+\frac{19.14}{R'^2}+\frac{174.7}{R'^4}+\cdots\right\}.$$

These coefficients, while more exact than (15), may be a little too small because they were derived variationally.

For He, ψ_0 may be approximated by Slater functions[31] of the type

$$\left(\frac{r}{a}\right)^{n-1}\exp\left(-\frac{Z-s}{n}\right)\frac{r}{a}$$

for each electron. Here, $Z-s=1.688$, $n=1$, and

$$(r^2)_{00}=1.05a^2,\quad (r^4)_{00}=2.79a^4.$$

On introducing these values into (14) we find

$$\Delta E_2=\frac{4}{R'^6}\frac{e^4}{a^2E_{\text{Av}}}\left\{0.739+\frac{5.86}{R'^2}+\frac{21.8}{R'^4}+\cdots\right\}.$$

If again we put $E_{\text{Av}}=$ twice the ionization energy of He, we obtain

$$\Delta E_2=-\frac{0.70}{R'^6}\left\{1+\frac{7.9}{R'^2}+\frac{30}{R'^4}+\cdots\right\}\times 10^{-10}\text{ ergs.} \tag{16}$$

A variational method (cf. Section C III) yields 0.68 in place of the factor 0.70, which shows that the replacement of E_{Av} by $2E_0$ is not quite permissible. The other terms, too, are affected by this error, but not necessarily in the same way. Page[32] has made a careful study of the dipole-quadrupole term in He. Using a variational method he calculated ΔE_2 without resorting to a Taylor expansion of the classical perturbation theory, and showed that its use is proper. His numerical dipole-quadrupole term is $6.26/R'^2$ in place of the $7.9/R'^2$. The last term in (16) rarely matters. Buckingham,[33] also using a variational method, finds $7.76/R'^2$ for the ratio of the second to the first term in braces.

At the van der Waals minimum for He, which occurs at about $R'=5.5$, the second term contributes $\frac{1}{4}$ as much as the first.

II. Interaction between two oscillators

A good deal of qualitative and semi-quantitative information can be derived from consideration of a simple molecular model: the simple harmonic oscillator. This example has already been treated several times,[1, 18, 34] but attention has always been confined to the dipole-dipole term. We wish to present briefly a more comprehensive treatment which allows us to estimate the relative magnitudes of the higher contributions in many instances.

Let us represent the two interacting molecules by two isotropic three-dimensional oscillators. The state function describing this system in its unperturbed state is a product of six factors, one for each coordinate, $(x_1\cdots z_2)$, of the form

$$H_n(\beta x)^{\frac{1}{2}}e^{-\beta x^2/2}\equiv\psi_n.$$

H_n here stands for the nth Hermite polynomial, and each coordinate is supposed to refer to the center of mass of its molecule. The parameter β measures the stiffness of the oscillators. It is related to the polarizability α and the classical frequency ν as follows:

$$\beta=e^2/\alpha h\nu. \tag{17}$$

As before, we regard the V of Eq. B (5) as the perturbation and calculate $\sum'|V_{0i}|^2/(E_0-E_i)$. The function for the lowest state is

$$\psi_0=(\beta/\pi)^{\frac{3}{2}}\exp\left[-\tfrac{1}{2}\beta(r_1{}^2+r_2{}^2)\right],$$

and $E_i = h\nu\sum(n+\frac{1}{2})$, the sum extending over the six quantum numbers associated with the six coordinates. The calculation of V_{0i} involves nothing but the elementary formulas for the oscillator matrix elements. It will be found that the first line of V causes ψ_0 to combine only with doubly excited states, the second line with triply and the third with quadruply excited states; the corresponding values of $E_0 - E_i$ are $2h\nu$, $3h\nu$, $4h\nu$. When the computation is carried out, one finds

$$\Delta E_2 = -\frac{3}{2}\frac{e^4}{R^6}\cdot\frac{1}{2h\nu\cdot\beta^2} - \frac{45}{4}\frac{e^4}{R^8}\cdot\frac{1}{3h\nu\cdot\beta^3} - \frac{315}{8}\frac{e^4}{R^{10}}\cdot\frac{1}{4h\nu\cdot\beta^4}\cdots$$

or, by use of (17)

$$\Delta E_2 = -\frac{3}{4}\frac{\alpha^2 h\nu}{R^6} - \frac{15}{4}\frac{\alpha^3(h\nu)^2}{e^2R^8} - \frac{315}{32}\frac{\alpha^4(h\nu)^3}{e^4R^{10}} - \cdots. \qquad (18)$$

This result is not sufficiently significant because we have assumed that each oscillator contains but a single charge. Suppose now that there are f charges, all vibrating with the same frequency ν. One can then see easily that (17) must be replaced by

$$\beta = fe^2/\alpha h\nu,$$

and all terms in the equation preceding (18) are multiplied by f^2. The result will then be, in place of (18),

$$\Delta E_2 = -\frac{3}{4}\frac{\alpha^2 h\nu}{R^6} - \frac{15}{4}\frac{\alpha^3(h\nu)^2}{fe^2R^8} - \frac{315}{32}\frac{\alpha^4(h\nu)^3}{f^2e^4R^{10}} - \cdots. \qquad (19)$$

If it is desired, ν may be eliminated from this equation by the relation

$$\nu = \frac{e}{2\pi}\left(\frac{f}{\alpha M}\right)^{\frac{1}{2}},$$

which is valid for oscillators, so that it reads

$$\Delta E_2 = -\frac{3}{4R^6}\hbar e\left(\frac{f\alpha^3}{M}\right)^{\frac{1}{2}} - \frac{15}{4R^8}\hbar^2\frac{\alpha^2}{M} - \frac{315}{32R^{10}}\frac{\hbar^3}{e}\left(\frac{\alpha^5}{fM^3}\right)^{\frac{1}{2}} - \cdots. \qquad (19a)$$

M is here, of course, the electron mass.

The model with whose aid this formula, recently proposed by the author,[35] was derived is indeed a highly idealized one. Its chief characteristic is that it possesses a single frequency. Now there are many molecules and atoms which absorb one frequency with overwhelming intensity in their normal state, namely those having a one-term dispersion formula. In a crude approximation their vibrating charges may perhaps be said to be bound by simple harmonic forces in their normal state. For these molecules the (single) f value may at once be obtained from the dispersion formula. Eq. (19) is of course not accurate even when applied to them; undoubtedly the errors in the second and third terms are greater than in the first because they involve higher moments of the frequency distribution. But knowledge of the rough magnitudes of these higher terms is often useful. In Table III are listed a number of coefficients computed with its use. In cases where the dipole-quadrupole coefficients are known from other sources, the second term of (19) agrees sufficiently well with them.

The first term of Eq. (19) amounts to London's formula (10) with which it agrees when Δ there is replaced by its equivalent, $h\nu$. The first term of (19a) has a great resemblance to a formula given by Slater and Kirkwood;[36] we shall return to it in the next section.

III. Variation theory of dispersion forces

Shortly after the appearance of London's work, an entirely different attack was made upon the problem of dispersion forces by Slater and Kirkwood.[36] Employing a variational method due chiefly to Hassé[37] they calculated the coefficients of R^{-6} for a number of molecules having spherical symmetry. Similar methods have been used frequently afterwards in connection with the problem of van der Waals forces; because of their fruitfulness we wish to discuss the essentials of Slater and Kirkwood's method in this review.

The general problem to which the present formalism provides an answer is the same as that of the perturbation theory: We are given a system with a Hamiltonian operator H_0, and we know the function ψ_0 describing its state, as well as its energy E_0 in that state; for

$$H_0\psi_0=E_0\psi_0. \tag{20}$$

A known perturbation is applied to H_0, changing it to H_0+V. The question is: what is the effect of this perturbation upon ψ and E? Or, in symbols, what are the solutions and eigenvalues of

$$H\psi=E\psi? \tag{21}$$

The answer given by perturbation theory is often unwelcome, for unless the first-order perturbation is finite—which is not the case in the problem of dispersion forces—the answer involves all V_{0i} and hence requires a knowledge of all ψ_i besides ψ_0. This knowledge is rarely available. The method to be described avoids this difficulty.

It makes use of the basic fact that the integral

$$\langle H\rangle_{\text{Av}}\equiv N^2\int\varphi^*H\varphi d\tau\geqq E, \tag{22}$$

where $$N=\left[\int\varphi^*\varphi d\tau\right]^{-\frac{1}{2}}$$

and this is true if φ is any continuous function. If it were chosen identical with the ψ satisfying Eq. (21), the equality sign would hold. In the Hassé method, one arbitrarily takes

$$\varphi=\psi_0(1+v), \tag{23}$$

where v is a function to be specified later, and so adjusted that the integral $\langle H\rangle_{\text{Av}}$ becomes a minimum. Let us first calculate $\langle H\rangle_{\text{Av}}$, using (23).

$H_{\text{Av}}=T_{\text{Av}}+U_{\text{Av}}$, in which U is the potential energy. But $T_{\text{Av}}=\sum_i\langle T_i\rangle_{\text{Av}}$, where

$$\langle T_i\rangle_{\text{Av}}=-(\hbar^2/2M_i)\langle\partial^2/\partial x_i^2\rangle_{\text{Av}}. \tag{24}$$

The summation here extends over all coordinates of the problem, and the M_i are the masses of the particles involved. Now it happens to be advantageous for our present purpose to transform $\langle\partial^2/\partial x_i^2\rangle_{\text{Av}}$. If we denote differentiations with respect to x by primes, we have

$$N^{-2}\left\langle\frac{\partial^2}{\partial x_i^2}\right\rangle_{\text{Av}}\equiv\int\varphi^*\frac{\partial^2}{\partial x_i^2}\varphi d\tau=\int\psi_0^*(1+v^2)\psi_0''$$
$$+\int\psi_0^*(1+v)[2v'\psi_0'+\psi_0v'']d\tau. \tag{25}$$

v is understood to be a real function. We now wish to prove that the last integral on the right reduces to $-\int\psi_0^*\psi_0v'^2d\tau$. To do this, we expand

$$\int\psi_0^*\psi_0v'^2d\tau=\int\psi_0^*\psi_0(1+v)'^2$$
$$=-\int(1+v)[\psi_0^*\psi_0(1+v)']'d\tau.$$

The last step follows by partial integration in which the integrated term vanishes. When the differentiations indicated in the final integral are carried out, it is clear that

$$\int\psi_0^*\psi_0v'^2d\tau=-\int(1+v)(2\psi_0^*\psi'v'+\psi_0^*\psi_0v'')d\tau.$$

Hence Eq. (25) may be written

$$N^{-2}\langle\partial^2/\partial x_i^2\rangle_{\text{Av}}=\int\psi_0^*(1+v)^2\psi_0''d\tau-\int\psi_0^*\psi_0v'^2d\tau,$$

and as a consequence of this and of (24),

$$N^{-2}\langle H_0\rangle_{\text{Av}}=\int\psi_0^*(1+v)^2H\psi_0d\tau$$
$$+\frac{\hbar^2}{2}\int\psi_0^*\psi_0\sum_i\frac{1}{M_i}\left(\frac{\partial v}{\partial x_i}\right)^2d\tau.$$

Now we recall that $H=H_0+V$, and that ψ_0 satisfies Eq. (20). With this substitution,

$$\langle H\rangle_{\text{Av}}=E_0+N^2\left\{[(1+v)^2V]_{00}\right.$$
$$\left.+\frac{\hbar^2}{2}\sum_i\frac{1}{M_i}\left[\left(\frac{\partial v}{\partial x_i}\right)^2\right]_{00}\right\}. \tag{26}$$

The two subscripts, 00, indicate as before matrix elements calculated with the function ψ_0.

Thus far our development has been perfectly general and free from approximations. $\langle H\rangle_{\text{Av}}$ is indeed an upper limit to the energy we seek. We can go another step further, and say that $\langle H\rangle_{\text{Av}}-E_0$ is an upper limit to the perturbation energy due to V. But this depends very clearly on the supposition that E_0 is the true eigenvalue, and ψ_0 the true eigenfunction of the unperturbed problem. In most applications of the present method, ψ_0 is only an *approximate* solution of Eq. (20). In that case the quantity $\langle H\rangle_{\text{Av}}-E_0$, computed from (26), loses its character as an upper limit; it may be in error either way, but is still in general a good approximation. We shall put

$$\Delta E=\langle H\rangle_{\text{Av}}-E_0$$

and make the further supposition that v^2 is negligible as compared with v. This may further impair the limit character of the result. Eq. (26) now yields

$$\Delta E=\frac{V_{00}+2(vV)_{00}+\dfrac{\hbar^2}{2}\sum_i\dfrac{1}{M_i}\left[\left(\dfrac{\partial v}{\partial x_i}\right)^2\right]_{00}}{1+v_{00}}. \tag{27}$$

(a) Polarizability

Calculation of the static polarizability is not only an instructive and simple application of the present method, but its result will also be needed in establishing a relation between van der Waals forces and polarizabilities. We consider an atom containing only closed shells of electrons and we simplify the problem at once by ignoring the contribution of the inner shells to the polarizability. This will introduce an unknown error with the heavier rare gases, but the error is small because the internal electrons are rigidly bound with respect to small perturbing forces. Let the number of electrons in the outer shell be N. When a constant electric field F is applied along the z axis, the additional potential energy is

$$V=Fe\sum_{i=1}^{N}z_i$$

z_i, the coordinate of the ith electron, is measured from the nucleus as origin.

ψ_0 will be very much idealized: we shall take it to be a product of individual electron functions, each of which has spherical symmetry. This is a good assumption for He, and not unreasonable for closed shells of electrons in general. As a consequence of it, $(x_i^2)_{00}=(y_i^2)_{00}=(z_i^2)_{00}$, for every i. Besides, it is true, of course, that $(x_i)_{00}=(y_i)_{00}=(z_i)_{00}=0$ for every i.

In calculating the quantities which appear in (27) one observes that $V_{00}=0$. v is an arbitrary function, to be fixed in accordance with the nature of the problem. The trick in Hassé's method is to let v be proportional to V and to fix the constant of proportionality by making E a minimum. In the present case, somewhat greater generality may even be achieved by putting

$$v=\sum_i\lambda_i z_i$$

in which the λ's are variation parameters. A few steps below, it will appear that every λ_i is proportional to F, the perturbing field, and therefore small. Hence it is proper, for small fields, to neglect $(v^2)_{00}$ against 1, which was done in arriving at Eq. (27). At the same time it is evident that the polarization energy in strong fields is not correctly given by that equation. There are indeed saturation effects which appear in the calculation when $(v^2)_{00}$ is retained.

$$(vV)_{00}=Fe\sum_{ij}\lambda_i(z_iz_j)_{00}=Fe\sum_i\lambda_i(z_i^2)_{00}.$$

Furthermore, $\partial v/\partial z_i=\lambda_i$, $v_{00}=0$; hence Eq. (27) takes the form

$$\Delta E=2Fe\sum_i\lambda_i(z_i^2)_{00}+(\hbar^2/2M)\sum_i\lambda_i^2. \tag{28}$$

If this expression is to be a minimum

$$\lambda_i=-(2MFe/\hbar^2)(z_i^2)_{00},$$

and this reduces Eq. (28) to

$$\Delta E=-(2M/\hbar^2)F^2e^2\sum_i(z_i^2)_{00}{}^2.$$

Finally, because $\Delta E=-\frac{1}{2}\alpha F^2$, we find

$$\alpha=(4Me^2/\hbar^2)\sum_i(z_i^2)_{00}{}^2. \tag{29}$$

(b) Dispersion forces

The dispersion forces between two molecules whose ψ_0-functions satisfy the conditions discussed are easily calculated by the same method. We now append subscripts to refer to the two molecules; ψ_0 is understood to be the product $\psi_0(1)\psi_0(2)$. Limiting ourselves to the dipole-dipole energy, we have

$$V=\sum_{ij}V_{ij};$$

$$V_{ij}=(e^2/R)(x_{1i}\cdot x_{2j}+y_{1i}\cdot y_{2j}-2z_{1i}\cdot z_{2j});$$

i runs from 1 to N_1, the number of electrons in the outer shell of 1, j from 1 to N_2, the number in the outer shell of 2. Observe that again $V_{00}=0$. We now put

$$v=\sum_{ij}\lambda_{ij}(x_{1i}x_{2j}+y_{1i}y_{2j}-2z_{1i}z_{2j})$$

in complete analogy with the former example. Then $v_{00}=0$.

$$(vV)_{00}=\frac{e^2}{R^3}\sum_{ijkl}[(x_{1i}x_{2j}+y_{1i}y_{2j}-2z_{1i}z_{2j})\lambda_{kl}\cdot$$
$$\times(x_{1k}x_{2l}+y_{1k}y_{2l}-2z_{1k}z_{2l})]_{00}$$
$$=\frac{e^2}{R^3}\sum_{ij}\lambda_{ij}[x_{1i}{}^2x_{2j}{}^2+y_{1i}{}^2y_{2j}{}^2+4z_{1i}{}^2z_{2j}{}^2]_{00}$$
$$=\frac{6e^2}{R^3}\sum_{ij}\lambda_{ij}(z_{1i}{}^2)_{00}(z_{2j}{}^2)_{00}.$$

The element $(z_{1i}{}^2)_{00}$ refers to the first atom alone and is the same quantity as that appearing in Eq. (29). Thus, to use (27), there remains only the calculation of $\sum_i[(\partial v/\partial x_i)^2]_{00}$. The summation index in this expression runs over all electron coordinates, $3(N_1+N_2)$ in number. We first consider the sum over all coordinates of molecule 1. Since $\partial v/\partial x_{1i}=\sum_j\lambda_{ij}x_{2j}$, and similarly for y and z, we find

$$\sum_{i=1}^{N_1}\left(\frac{\partial v}{\partial x_{1i}}\right)^2+\left(\frac{\partial v}{\partial y_{1i}}\right)^2+\left(\frac{\partial v}{\partial z_{1i}}\right)^2$$
$$=\sum_{i=1}^{N_1}\sum_{j,k=1}^{N_2}\lambda_{ij}\lambda_{ik}(x_{2j}x_{2k}+y_{2j}y_{2k}+4z_{2j}z_{2k}).$$

The 0-0-element of this quantity is simply

$$\sum_{i=1}^{N_1}\sum_{j=1}^{N_2}\lambda_{ij}{}^2[(x_{2j}{}^2)_{00}+(y_{2j}{}^2)_{00}+4(z_{2j}{}^2)_{00}]$$
$$=6\sum_{ij}\lambda_{ij}{}^2(z_{2j}{}^2)_{00}.$$

The remainder of the summation yields the matrix element $6\sum_{ij}\lambda_{ij}{}^2(z_{1i}{}^2)_{00}$, and it is the sum of these two expressions which appears in Eq. (27). This now reads:

$$\Delta E=12\sum_{ij}\left\{\frac{e^2}{R^3}\lambda_{ij}(z_{1i}{}^2)_{00}(z_{2j}{}^2)_{00}\right.$$
$$\left.+\frac{\hbar^2}{4M}\lambda_{ij}{}^2[(z_{1i}{}^2)_{00}+(z_{2j}{}^2)_{00}]\right\}.$$

If it is to be a minimum, every

$$\lambda_{ij}=-\frac{2e^2M}{R^3\hbar^2}\frac{(z_{1i}{}^2)_{00}(z_{2j}{}^2)_{00}}{(z_{1i}{}^2)_{00}+(z_{2j}{}^2)_{00}},$$

so that

$$\Delta E=-\frac{12M}{\hbar^2}\frac{e^4}{R^6}\sum_{ij}\frac{(z_{1i}{}^2)_{00}{}^2(z_{2j}{}^2)_{00}{}^2}{(z_{1i}{}^2)_{00}+(z_{2j}{}^2)_{00}}. \qquad (30)$$

In going on from here toward numerical evaluation of the matrix elements the ψ_0-functions have to be specified completely. For heavier atoms, the Pauli principle has to be taken into account; i.e., the ψ_0-functions must be written in determinantal form. Details may be found in the work of Hellmann and Buckingham discussed below.

It is perhaps more interesting to seek a relation between (30) and (29) from which the matrix elements are eliminated. This can be done if we make one further simplifying assumption, indeed one which is strongly suggested by those already made: that all matrix elements $(z_{1i}{}^2)_{00}$ be equal, regardless of i; and similarly for the $(z_{2j}{}^2)_{00}$. Restriction to a single closed shell was necessary chiefly to make this assumption plausible. Eq. (29) now reads

$$\alpha=4NMe^2(z^2)_{00}{}^2/\hbar^2 \qquad (31)$$

and (30) becomes

$$\Delta E=-\frac{3}{2R^6}\frac{e\hbar}{(M)^{\frac{1}{2}}}\frac{\alpha_1\alpha_2}{(\alpha_1/N_1)^{\frac{1}{2}}+(\alpha_2/N_2)^{\frac{1}{2}}}, \qquad (32)$$

or, if the molecules are similar,

$$\Delta E=-\frac{3}{4}\frac{e\hbar}{R^6}\left(\frac{N\alpha^3}{M}\right)^{\frac{1}{2}}. \qquad (32')$$

This formula is due to Slater and Kirkwood.[36, 38] In Table III may be found values of the dipole coefficient computed from it. Agreement between these and the results of London's formula (10) is not always good, even when a one-term dispersion formula describes the index of refraction quite well. It seems that it is impossible to assign general superiority to either (10) or (32), for both contain uncontrollable errors due to simplifications. Only for atomic hydrogen does (30) carry assurance of representing an upper limit.

An interesting side light falls on the Slater-Kirkwood formula from the developments of the preceding section. Eqs. (19) and (19′) show that, for a simple oscillator, the latter formula becomes identical with London's. They remain identical for molecules with a single absorption frequency if N in the Slater-Kirkwood formula is replaced by f. The reason why the latter gives larger results than London's is simply that f is always smaller than N. Now N is a rather doubtful quantity, as the derivation of Eq. (32) has shown, and one wonders whether the insertion of an experimentally determined f might not represent a better approximation.

The analysis leading to Eq. (32) has been entirely without refinements, and stands definitely in need of generalization. In the first place, one should include the inner shells of the molecules. This, according to Hellmann,[39] leads to the formula

$$\Delta E = -\frac{3}{2}\frac{e\hbar}{(M)^{\frac{1}{2}}}\sum_{ij}\frac{\alpha_i\alpha_j}{(\alpha_i/n_i)^{\frac{1}{2}}+(\alpha_j/n_j)^{\frac{1}{2}}}$$

in place of (32), where i labels the *subshells* of molecule 1, j those of molecule 2, and n_i and n_j are the numbers of electrons in each subshell. The result is obtained in the same manner as (32), the only change being the use of one variation parameter λ_i for every shell, λ_{ij} for every pair of shells. Hellmann did not permit exchange between the electrons in different shells, but Buckingham,[40] in a more complete analysis, showed that inclusion of exchange does not alter the final result, though it gives better numerical values for the polarizability.

Another atomic property, the atomic diamagnetic susceptibility, is sometimes drawn into the discussion.[37, 41] The advantage gained thereby lies in the fact that the resulting expression for the dispersion forces no longer contains the ambiguous number N. A simple procedure is the following. χ, the diamagnetic susceptibility, is given by the formula:

$$\chi = (e^2/2Mc^2)\sum_i(z_i)_{00}. \tag{a}$$

Under the assumptions of our analysis, therefore,

$$(z_i^2)_{00} = (2Mc^2/Ne^2)\chi. \tag{b}$$

Since, from (31),

$$(z^2)_{00} = \hbar^2\alpha/4MNe^2, \tag{c}$$

we can form an expression for $(z^2)_{00}$ which is free from N by combining (b) and (c):

$$(z^2)_{00} = \hbar^2\alpha/8M^2c^2\chi. \tag{d}$$

But Eq. (30) may be written

$$\Delta E = -\frac{12MN_1N_2e^4}{\hbar^2R^6}\frac{(z_1^2)_{00}^2(z_2^2)_{00}^2}{(z_1^2)_{00}+(z_2^2)_{00}}. \tag{e}$$

We express the elements in the numerator by relation (c) and in the denominator by (d), obtaining

$$\Delta E = -\frac{6Mc^2}{R^6}\frac{\alpha_1\alpha_2}{\alpha_1/\chi_1+\alpha_2/\chi_2}. \tag{f}$$

One can see that this result is not likely to be very precise. Eq. (a) is an exact expression, Eq. (e), however, very approximate. Thus cancellation of errors is impossible. But partial cancellation of errors takes place when an approximate expression for α, like (29), derived by the same method as (e), is substituted in (e), and that is the reason why (32) represents a better approximation than Eq. (f) here deduced. London[1] shows that the use of (f) leads to values which disagree very much with those derived with the use of his formula C (10). The reason for the discrepancy is the fact that the physical mechanism to which dispersion forces owe their existence is quite different from the interaction of electrons with a magnetic field, and that the use of empirical matrix elements of the type $(\sum_i z_i)_{0\lambda}^2$, i.e., f values, is therefore more natural to the problem than the emphasis on $\sum_i(z_i^2)_{00}$, i.e., susceptibilities.

IV. Additivity of dispersion forces

Many applications of van der Waals forces, in particular to the problems of surface tension of liquids, heats of sublimation of crystals, require them to be additive. Attention has been called in the introduction to the additivity of forces due to the induction effect. This property is not shared entirely by the alignment forces between polar molecules, and it is absent in all first-order interactions between them. The dispersion effect, however, is additive,[18c] as one may easily show by the perturbation method.

Forces are said to be additive when the total energy of interaction of n particles is composed from the energy of pairs, ΔE_{ij}, as follows:

$$\Delta E = \sum_{i>j} \Delta E_{ij}. \tag{33}$$

We shall show that this relation holds for all interactions derivable by second-order perturbation theory, provided the classical interaction has the property of additivity.

Consider n molecules, sufficiently far apart so that the state function may be written

$$\Psi_k = \psi(k_1)\psi(k_2)\cdots\psi(k_n),$$

in which k is the set of all quantum numbers of the pth molecule. They are subject to a perturbation

$$V = \sum_{i>j} V(ij).$$

i and j here denote all coordinates pertaining to the ith and jth molecules. In our case $V(ij)$ is the Coulomb energy between molecules i and j, and these, as we know, add in the manner (33). We wish to calculate

$$\Delta E_2 = \sum_{\kappa_1\cdots\kappa_n} \frac{\int \Psi_k^* V \Psi_\kappa d\tau}{\sum_{p=1}^{n} E(k_p) - E(\kappa_p)}. \tag{34}$$

But because of the orthogonality of the $\psi(k_p)$ for different p, and because $V(ij)$ contains only the coordinates of two molecules,

$$\int \Psi_k^* V \Psi_\kappa d\tau = \sum_{i>j} (k_i k_j | V | \kappa_i \kappa_j) \prod_{s \neq i,\, j} \delta(k_s \kappa_s).$$

If this expression is inserted in (34) the result is

$$\Delta E_2 = \sum_{i>j} \sum_{\kappa_i\kappa_j}{}' \frac{|(k_i k_j | V | \kappa_i \kappa_j)|^2}{E(k_i) + E(k_j) - E(\kappa_i) - E(\kappa_j)}.$$

The sum $\sum'$, however, is simply the interaction energy ΔE_{ij}, hence the proof of Eq. (33) is completed. It amounted merely to showing that the property of additivity, possessed by the classical potential, is not lost in the quantum-mechanical manipulations.

It is clear at the outset that first-order interactions do not share the simplicity expressed by Eq. (33). For they are the roots of secular equations which are in general irrational.

V. Relative magnitudes of effects

Brief comment should be made about the relative magnitudes of the various effects treated so far. It is already clear that atoms possessing no permanent asymmetry of charge distribution exhibit only the dispersion effect; if these atoms exist in states other than the S states a weak first-order force of the type B(36) is superposed on the latter. But molecules having permanent moments are subject in general to dispersion, alignment and induction effects. This distinction is really historical, for we have seen that all three spring from the same root: The dispersion effect is obtained if, in the second-order perturbation formula, the summation is extended only over matrix elements corresponding to large (electronic and vibrational) energy differences; the alignment effect, by summing only over small (rotational) energy differences; the induction effect involves summing over large differences in one and small differences in the other molecule.[18c] To the extent that rotational energies may be neglected against electronic energies, the three effects may simply be added when occurring simultaneously. Tables of numerical values may be found elsewhere.[1, 18b] (Cf. also Table IV.) Of the molecules for which data are available, those having dipole moments $\leqq 10^{-18}$ e.s.u. exhibit induction and alignment effects so weak that they are practically negligible in comparison with the dispersion effect. The induction effect is insignificant in all known cases. For NH_3 alignment and dispersion effects are about equal in magnitude; for H_2O and HCN the former predominates strongly.

The question finally arises as to the magnitude of purely magnetic interactions. The electron spins produce first-order forces proportional to R^{-3} unless they are paired within a molecule. A simple example will suffice to show their order of magnitude. An H-atom in its normal state exerts dispersion forces upon a similar atom, given approximately (C-Ib) by

$$|\Delta E| \approx 3p^4/E_0R^6,$$

where $p = ea$, the instantaneous dipole moment of the atom, and $E_0 = -e^2/2a$. The magnetic interaction energy

$$|\Delta E_m| \approx \mu^2/R^3,$$

where $\mu = \frac{1}{2}\alpha p$, and $\alpha = 1/137$, the fine structure constant. The ratio

$$\frac{|\Delta E_m|}{|\Delta E|} = \frac{\alpha^2}{12} \frac{E_0}{p^2} R^3 = \frac{\alpha^2}{24}\left(\frac{R}{a}\right)^3.$$

This is greater than unity if $R > 75a = 40\text{A}$. But at these large distances one is rarely interested in van der Waals forces. It is also to be remembered that these forces vanish on the average over all orientations.

Forces due to orbital magnetic moments are of the same order of magnitude and hence may also as a rule be ignored.

D. FORCES BETWEEN EXCITED MOLECULES

The weak quadrupole forces between molecules and atoms not in states of spherical symmetry have already been discussed (B, IIc). They properly belong in this section as well. In addition, there are two much stronger kinds of interaction to be considered when one or both of the molecules are in excited states. They are: (1) resonance between electronic states and (2) dispersion forces of the type discussed above, but with new and interesting properties.

I. Resonance forces

The condition of resonance between rigid dipoles has already been studied (B-IIa). It arises when one molecule is capable of emitting a quantum of energy which may be received by the other. In the case of rigid dipoles the quantum is of infra-red frequency, but the situation of resonance may clearly be much more general. Its most interesting example is the interaction of two molecules or atoms, one of which is in its normal state, the other in an excited state which combines strongly—by emission of radiation—with the normal state, for instance the state from which the "resonance line" can be emitted.

Let us consider the case of two similar atoms, one in its normal state (with $L=0$), the other one in an excited state (with $L=1$). There will then be resonance degeneracy between the two functions

$$\Psi_1 = \psi_0(1)\psi_1(2) \quad \text{and} \quad \Psi_2 = \psi_1(1)\psi_0(2).$$

The perturbing potential is taken at present in the form C(4), and the matrix elements between Ψ_1 and Ψ_2 are at once seen to be

$$V_{11} = V_{22} = 0;$$

$$V_{12} = V_{21} = (e^2/R^3)\{|X_{01}|^2 + |Y_{01}|^2 - 2|Z_{01}|^2\},$$

the subscripts on X, Y and Z referring now to the states of a single atom. On referring back to the definition of f values, Eq. C(1), we observe that the V elements may be written

$$V_{12} = V_{21} = \frac{3}{2R^3} \frac{(\hbar e)^2}{M(E_1 - E_0)} \{f_{01}{}^x + f_{01}{}^y - 2f_{01}{}^z\}. \quad (1)$$

The secular equation reads

$$\begin{vmatrix} -\Delta E & V_{12} \\ V_{12} & -\Delta E \end{vmatrix} = 0,$$

and its solutions are

$$\Delta E = \pm V_{12}. \quad (2)$$

To evaluate Eq. (1) explicitly it is necessary to know the value of the magnetic quantum number associated with ψ_1. If $m = +1$ or -1, $f^x = f^y$ and $f^z = 0$; if $m = 0$, $f^x = f^y = 0$. A glance at the matrix elements of X, Y, Z [II, (15)] shows that the resonance forces are twice as strong when $m = 0$ as when $m = \pm 1$, a fact easily connected with the charge distribution of the excited atom: when $m = 0$, the long axis of the distribution points toward the unexcited atom: when $m = \pm 1$ it stands across the line connecting the atoms.

The mean of ΔE over all three values of m vanishes, because the mean of V_{12} is zero as Eq. C(3) shows.

Assignment of definite values of m has meaning only when a magnetic field is present. Strictly speaking, therefore, the degeneracy with respect to space quantization should have been considered in setting up the secular equations. We have not done so here, for the result would be the same.

An extension of the present analysis to more complicated cases is hardly necessary. The main features of resonance forces are: (1) they are proportional to $1/R^4$; (2) their strength is proportional to the f value of the transition connecting the two resonance states; (3) they vanish in the mean over all m values and (4) numerically, they are of the order 100 times as strong as the dispersion forces near the closest distance of approach. Resonance forces are ***not*** additive, which is at once apparent when an attempt is made to solve the secular determinant for more than two atoms.

II. Dispersion forces between excited atoms, anisotropy

Forces between excited atoms are of primary interest in connection with the problem of pressure effects on spectral lines. As might well be expected, they are of a complicated nature and not amenable to general treatment.

We recall first that London's formula, C(7), is applicable to excited states as well as normal states. But it gives only the mean of all interactions, taken over all quantum numbers m_1 and m_2. This mean interaction is not always negative as it was found to be for the normal states; in general the denominators will change signs irregularly, and the forces may well become repulsive. But the forces depend also on the orientation of the excited atom.

To see the main features of the situation we calculate in detail the dispersion effect between an atom in an S state and another one in a P state, each having a single valence electron. The calculation will be restricted to dipole-dipole forces. As in C-I, we are led to Eq. C(5). In expanding it, the cross terms in the square may be omitted for the same reason as before; hence

$$\Delta E_2=\frac{e^4}{R^6}\sum_{\substack{\kappa_1\mu_1\\ \kappa_2\mu_2}}{}' \frac{\begin{array}{r}|(1m_1|x_1|\kappa_1\mu_1)|^2|(00|x_2|\kappa_2\mu_2)|^2+|(\cdots|y_1|\cdots)|^2|(\cdots|y_2|\cdots)|^2\\ +4|(\cdots|z_1|\cdots)|^2|(\cdots|z_2|\cdots)|^2\end{array}}{E(1)+F(0)-E(\kappa_1)-F(\kappa_2)}.$$

Here the P state of atom 1 is designated by $(1,m)$, the values of l and m; the S state of atom 2 by $(0,0)$; the energies of one are labeled E, the others F. In carrying out the summation over μ_1 and μ_2 we observe the following relations, easily derived with the use of B(15):

$$\sum_\mu |(00|x|\kappa\mu)|^2=\sum_\mu |(00|y|\kappa\mu)|^2$$

$$=\sum_\mu |(00|z|\kappa\mu)|^2=\tfrac{1}{3}r_{0\kappa}{}^2\delta(l_\kappa 1),$$

$$\sum_\mu |(1m|x|\kappa\mu)|^2=\sum_\mu |(1m|y|\kappa\mu)|^2$$

$$=r_{1\kappa}{}^2\left[\frac{m^2}{6}\delta(l_\kappa 0)+\frac{6+m^2}{30}\delta(l_\kappa 2)\right],$$

$$\sum_\mu |(1m|z|\kappa\mu)|^2=r_{1\kappa}{}^2\left[\frac{1-m^2}{3}\delta(l_\kappa 0)+\frac{4-m^2}{15}\delta(l_\kappa 2)\right],$$

l_κ is the l value associated with state κ. When these are substituted,

$$\Delta E_2=\frac{e^4}{R^6}\left\{\frac{4-3m^2}{9}\sum_{\kappa_1\kappa_2}{}_1\frac{(1|r_1|\kappa_1)^2(0|r_2|\kappa_2)^2}{E(1)-E(\kappa_1)+F(0)-F(\kappa_2)}\right.$$

$$\left.+\frac{22-3m^2}{45}\sum_{\kappa_1\kappa_2}{}_2\frac{(1|r_1|\kappa_1)^2(0|r_2|\kappa_2)^2}{E(1)-E(\kappa_1)+F(0)-F(\kappa_2)}\right\}. \quad (3)$$

Two different summations are here written; $\sum_1$ extends over all states κ_2 for which $l=1$, and all states κ_1 for which $l=0$; $\sum_2$ extends over states k_2 with $l=1$, κ_1 with $l=2$. These sums are independent of m, the space quantum number of the excited atom. To evaluate Eq. (3) for a real atom would require a considerable amount of labor which is hardly worth while. What might happen can be seen by applying it to the oscillator model already discussed in C-II.

In that case each sum reduces to a single term, and simple calculation gives in place of Eq. (3)

$$\Delta E_2=-\frac{e^4}{R^6}\frac{\hbar^4}{M^2h\nu_1\cdot h\nu_2}\left\{\frac{1-\frac{3}{4}m^2}{h\nu_2-h\nu_1}+\frac{\frac{11}{6}-\frac{1}{4}m^2}{h\nu_2+h\nu_1}\right\}.$$

TABLE III. *Dispersion forces. Values in ( ) are uncertain.*
$\Delta E_2 = -c_1R^{-6} - c_2R^{-8} - c_3R^{-10} - \cdots$

	$h\nu$ (ev)	$\alpha \times 10^{24}$ cm^3	f	$c_1 \times 10^{60}$ (erg·cm^6)	$c_2 \times 10^{76}$ (erg·cm^8)	$c_3 \times 10^{92}$ (erg·cm^{10})	Reference
H				6.098	32.60	83.09	1
He	24.5	0.205		1.49			2
				1.23			3
				1.63	3.53		4
				1.52	3.35		5
		0.205	1.1	1.23	1.89	1.65	6
Ne				7.97			2
				7.48	10.9		4
	25.7	0.39	2.37	4.67	6.9	5.3	6
A				69.5			2
				63.5	190		4
	17.5	1.63	4.58	55.4	120	136	6
Kr				129			2
				136	420		4
	14.7	2.46	4.90	107	275	370	6
Xe				273			2
	12.2	4.0	5.61	233	710	1,120	6
H_2	(14.5)	0.81	(1.5)	11.4	31	45	6
N_2	15.8	1.74	4.61	57.2	120	130	6
O_2	13.6	1.57	3.11	39.8	96	120	6
CO_2	15.5	2.86	5.70	152	410	590	6
CH_4	14.1	2.58	4.60	112	310	440	6
NH_3	11.7	2.24	2.72	70	236	410	6
Cl_2	12.7	4.60	6.55	321	1,000	1,630	6
HCl	13.4	2.63	4.25	111	320	480	6
HBr	12.1	3.58	4.71	185	600	1,000	6
HI	10.5	5.4	5.30	370	1,360	2,700	6
Na	2.08	29.7	1	2,190	47,600	530,000	6
K	1.60	(49)	(1)	4,600	127,000	1,800,000	6

[1] L. Pauling and J. Y. Beach, Phys. Rev. **47**, 686 (1935).
[2] J. C. Slater and J. G. Kirkwood, Phys. Rev. **37**, 682 (1931).
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[5] Eq. C(16).
[6] Eq. C(19).

ν_1 and ν_2 are the classical frequencies of the oscillators. The first term here reminds again of the possibility of resonance for which the present theory breaks down. It also shows that if the frequency of the unexcited is smaller than for the excited atom the first term in braces is negative; since it depends rather strongly on m, a change in m from 0 to ± 1 may cause the forces to change from repulsion to attraction. This represents an approach to the condition of resonance discussed under I. The entire behavior also shows that dispersion forces are not to be thought of as central forces; indeed they are central only when the attracting molecules have spherical charge distribution and behave other-

TABLE IV. *Induction and orientation effects (after London).*

	$\mu \times 10^8$	Alignment (Orientation)	Induction	Dispersion
CO	0.12	0.0034	0.057	67.5
HI	0.38	0.35	1.68	382
HBr	0.78	6.2	4.05	176
HCl	1.03	18.6	5.4	105
NH_3	1.5	84	10	93
H_2O	1.84	190	10	47

wise very much like polar forces superposed on central ones. The anisotropy of dispersion forces for complex molecules having different polarizabilities along different axes is discussed by de Boer and Heller.[42]

Of course it is possible to write Eq. (3) in terms of f values, also. It then becomes

$$\Delta E_2 = \frac{3}{4R^6}\frac{(\hbar e)^4}{M^2} \times \left\{ (4-3m^2) \sum_{\kappa_1\kappa_2}{}_1 \frac{f(1,\kappa_1)f(0,\kappa_2)}{E(1)-E(\kappa_1)+F(0)-F(\kappa_2)} + \frac{22-3m^2}{10} \sum_{\kappa_1\kappa_2}{}_2 \frac{f(1,\kappa_1)f(0,\kappa_2)}{E(1)-E(\kappa_1)+F(0)-F(\kappa_2)} \right\} \cdots. \quad (4)$$

When the mean over the three values of m is taken, the factors of the sums both become 2, and London's formula results.

Inaccurate knowledge of the f values associated with excited states prevents us at present from making exact use of the formulas developed in this section. Rough estimates for various cases of interest have been made by the author and may be found in reference 43. It would be easy to obtain formulas similar to (4) for the interaction of two molecules both of which are excited. But the use which could be made of them is so limited that we shall forego writing them down.

E. Tables of Calculated Constants

Table III represents a list of constants calculated for dispersion forces. Multiple entries are made wherever the coefficients have been computed by different methods, the intention being mainly to show what numerical discrepancies remain among the various methods. It will be observed that the variational results (Slater and Kirkwood, Buckingham) are always greater than those based on empirical f values (London and Eq. C(19)). It seems likely that the true values lie between the two. We also expect the coefficients c_2 and c_3, as deduced from Eq. C(19), to be smaller than the correct ones.

For the sake of convenience we list the conversion factors from the absolute units employed in Table III to Hartree (atomic) units.

c_1 (erg·cm^6) $= 9.38\times10^{-61}$ (atomic units),
c_2 (erg·cm^8) $= 2.62\times10^{-77}$ (atomic units),
c_3 (erg·cm^{10}) $= 7.32\times10^{-94}$ (atomic units).

It should be noted that the coefficients c_2 and c_3 for Na and K are abnormally large. Dipole-quadrupole forces are equal to the dipole-dipole forces at approximately $R=5$A. Consequently, convergence fails even at these relatively large distances, and the usual formalism cannot be employed.

Finally, we wish to point out that the ratio, c_2/c_1, which determines the value of R beyond which quadrupole forces may be neglected, does not fluctuate as widely among the different theories as do the coefficients themselves. The quantity c_2/c_1 in the units of Table III, incidentally, is the ratio of dipole-quadrupole to dipole-dipole energy at a hypothetical distance of 1A.

Table IV is taken from London's article.[1] It shows the relative magnitudes of the three main effects contributing to the van der Waals forces. The column labeled "Alignment (Orientation)" contains the coefficient of R^{-6} in formula B(7) for $T=293°$; the next gives the corresponding coefficient, $2\alpha p^2$, in formula B(10); the last c_1. All coefficients are in units: 10^{60} erg cm^6. c_1 differs slightly from the values in Table III because of different choices for $h\nu$.

F. Summary of Applications

As stated in the introduction, our concern in this article was with the fundamental theory of van der Waals forces. This limitation has forced us to omit from consideration many matters dealing primarily with applications, but having an essential bearing on theory. Notable among these is the work of Mayer[44] who, in dealing with the binding energies of ionic crystals, calculated the dispersion forces between a number of ions having closed shells of electrons. His method is based on Eq. C(7), but the procedure is interesting inasmuch as it involves an integration over the frequencies of the continuous spectrum whose contribution for ions is large. A similar procedure had been used in a determination of the dispersion forces between He atoms.[45]

To aid the reader who wishes to inform himself of the many applications which the theory has induced or by which it has been corroborated, we append here a list of references to articles of relevance in this connection. Though this list is meant to be fairly complete, one can hardly dare hope that no important papers have been omitted.

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